Grazing Incidence Small Angle X-ray Scattering

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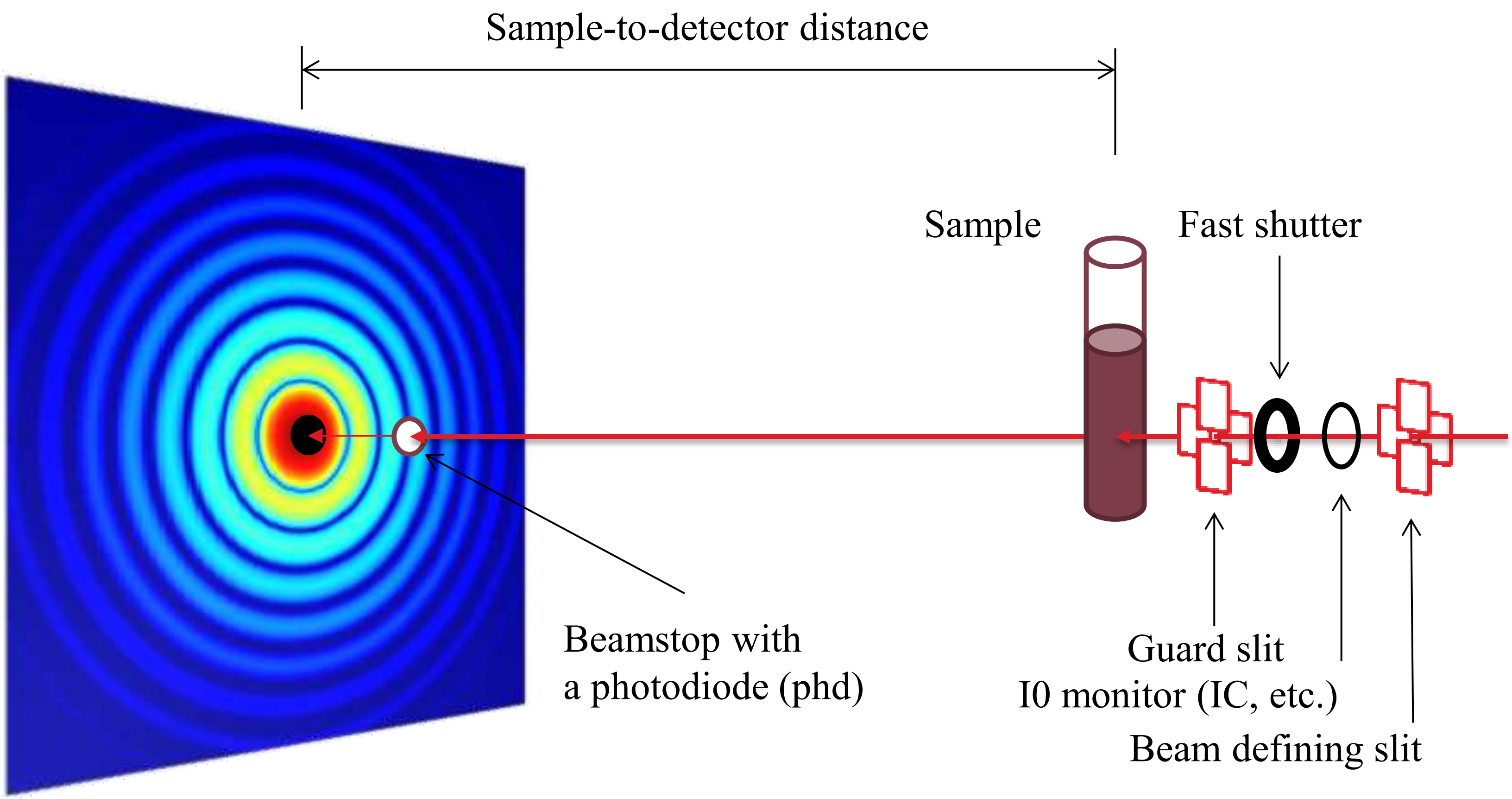
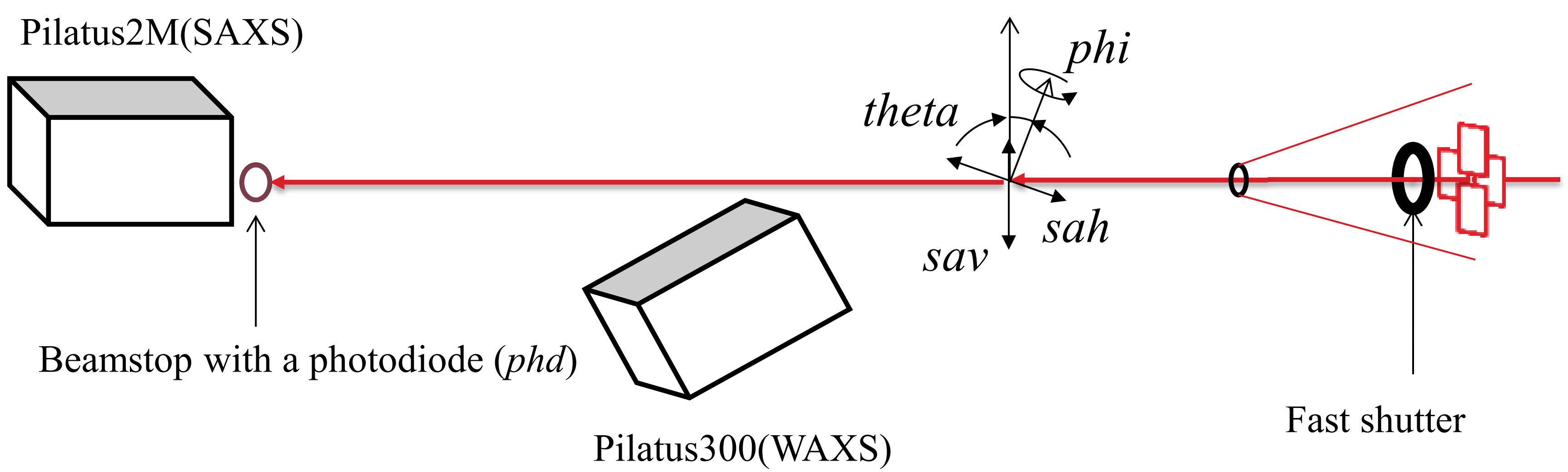
Outline

- Grazing Incidence Small Angle X-ray **Scattering** (GISAXS) beamline and setup
- Key knowledge to interpret GISAXS
  - Fourier Transform
  - Shape, size, and orientation of particles and lattices
- The effect of a small incident angle
  - Reflection
    - Experimental examples: Crystalline nano particles.
  - Penetration depth
    - Experimental examples: Block copolymer films
  - Refraction
- Grazing Incidence Small Angle X-ray **Diffraction**
  - Ewald sphere
    - Experimental examples: Block copolymer films
- Quantitative calculation
  - Distorted wave Born approximation
  - Snell’s law and Fresnel’s law

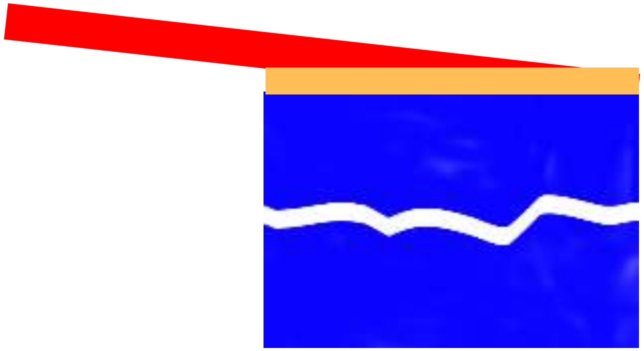

Sample-to-detector distance
Sample
Fast shutter
Beamstop with
a photodiode (phd)
Guard slit
I0 monitor (IC, etc.)
Beam defining slit


Pilatus2M(SAXS)
phi
theta
sah
sav
Beamstop with a photodiode (phd)
Pilatus300(WAXS)
Fast shutter

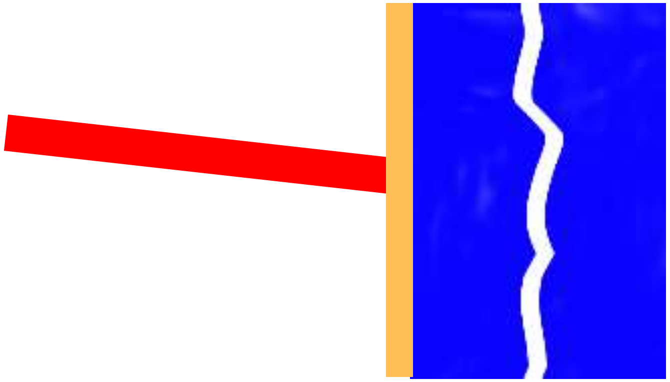
12ID-B beamline at APS

Why GISAXS?

GISAS

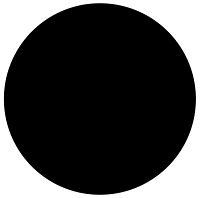


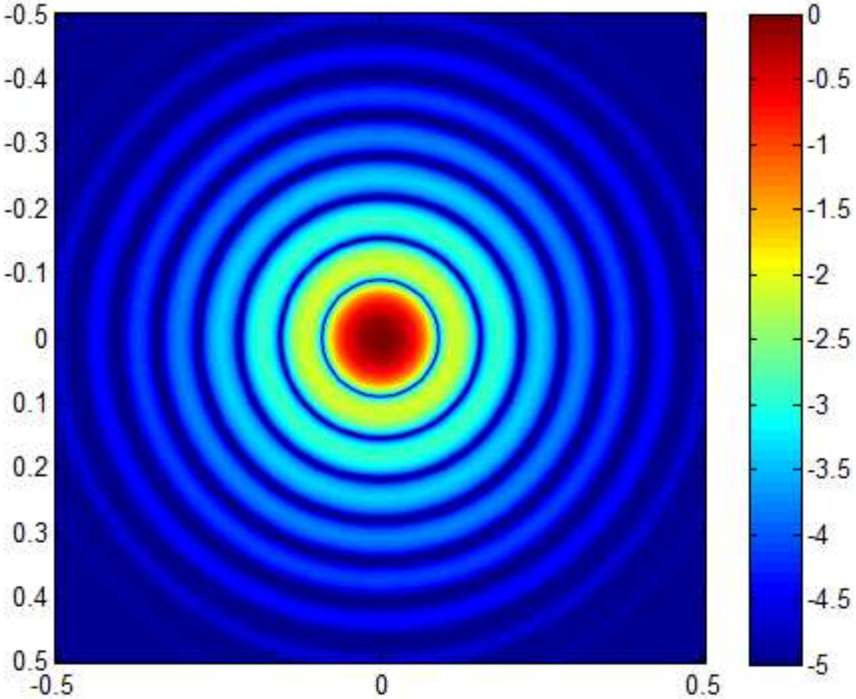
SAS



Advantage for the grazing incidence geometry for thin film.
1. Several orders larger scattering volume
2. Scatterings from oriented samples

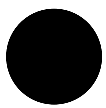
Scattering and Fourier Transform

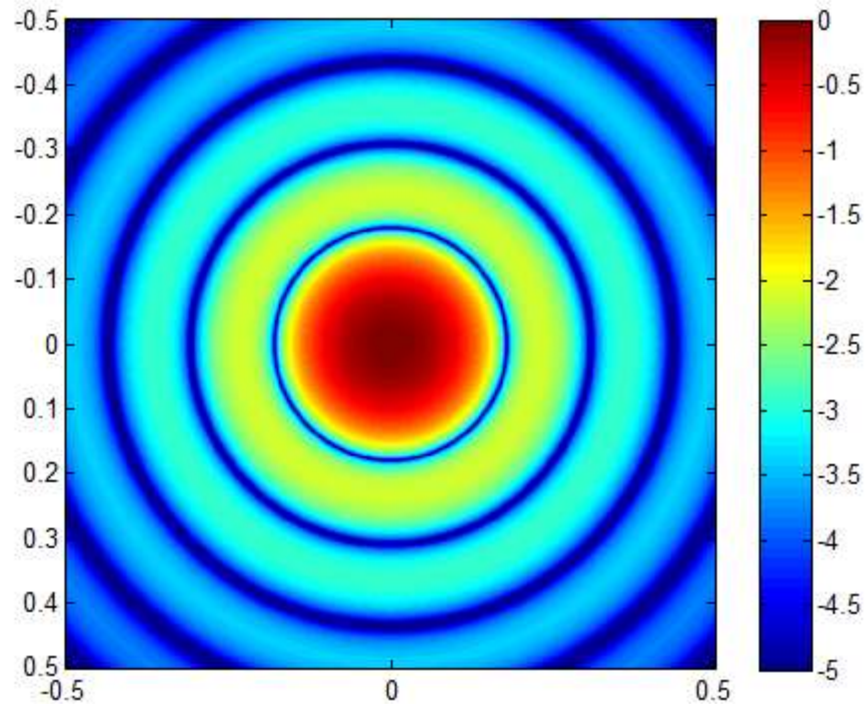




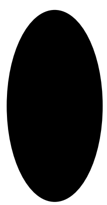
Electron density

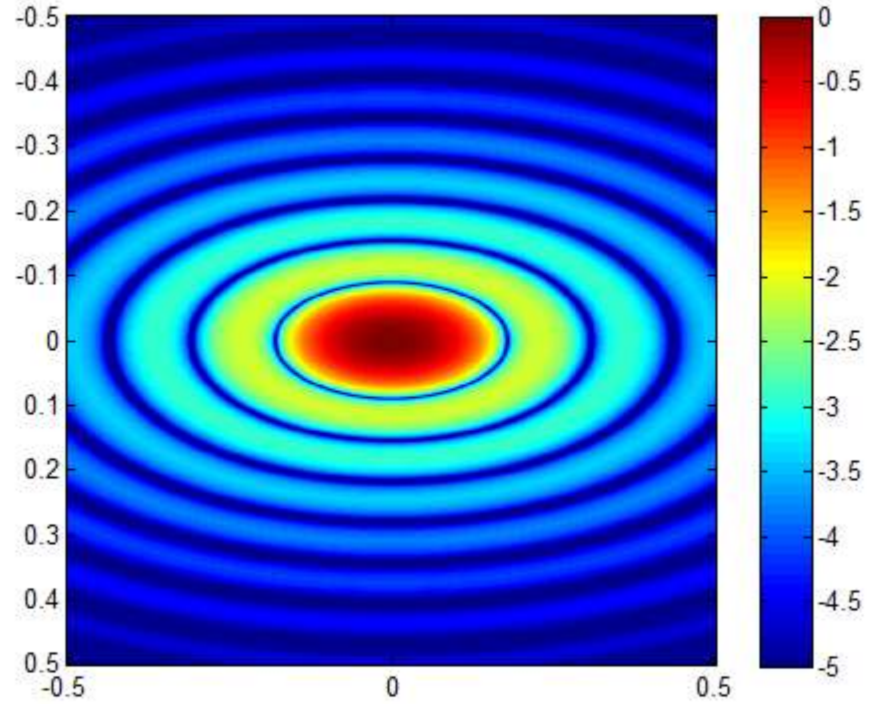
|FT(Electron density)|^2



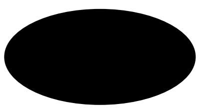


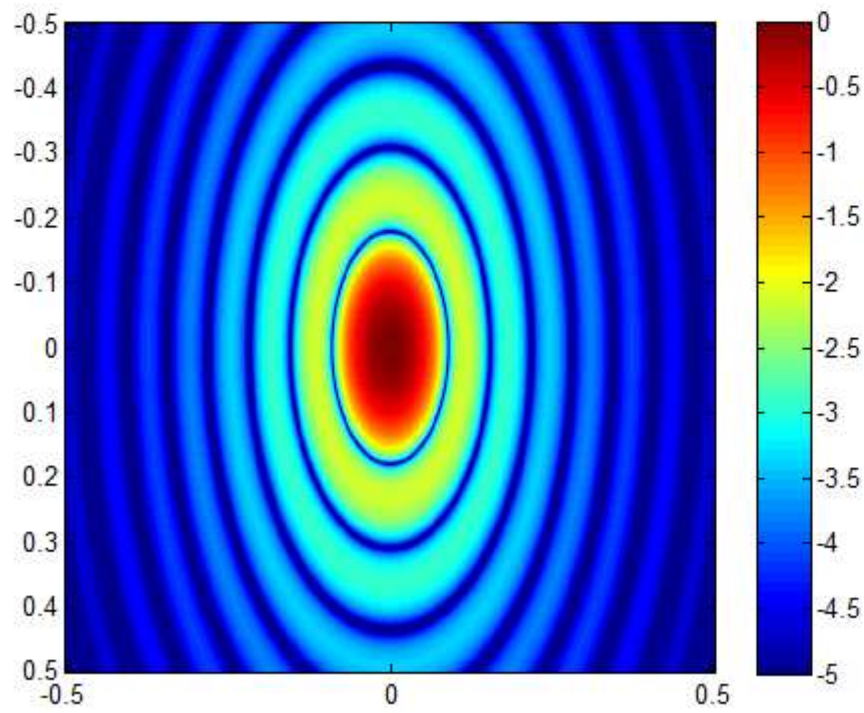
The Bragg equation: $q = 2\pi/D$





1. The Bragg equation: $q = 2\pi/D$
2. Orientation

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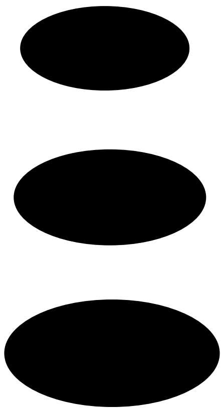
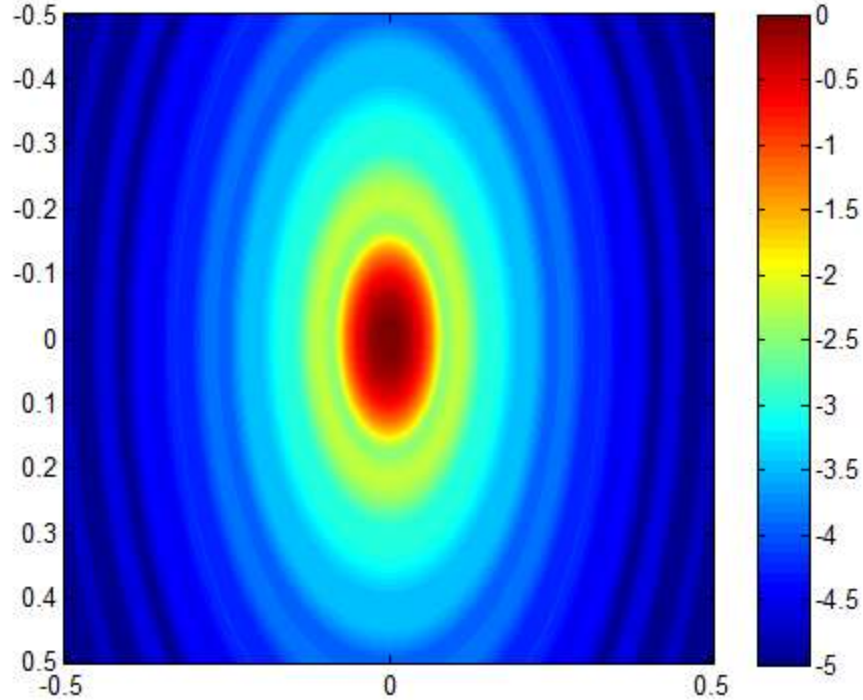
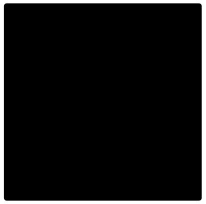
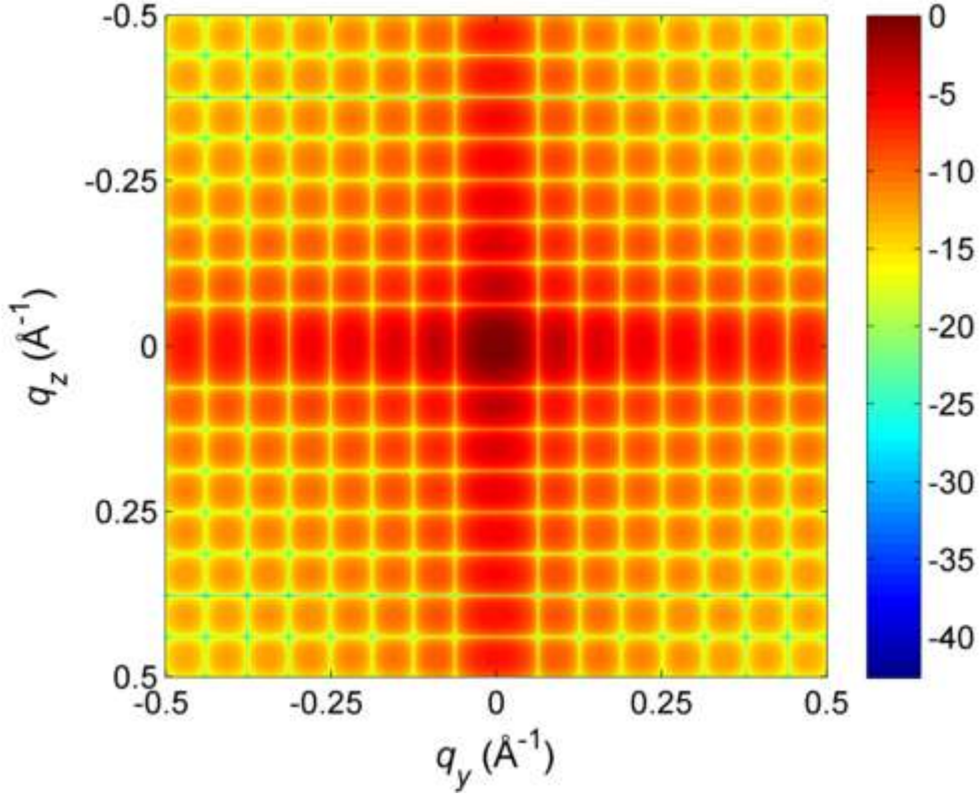
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
-0.5
0
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5



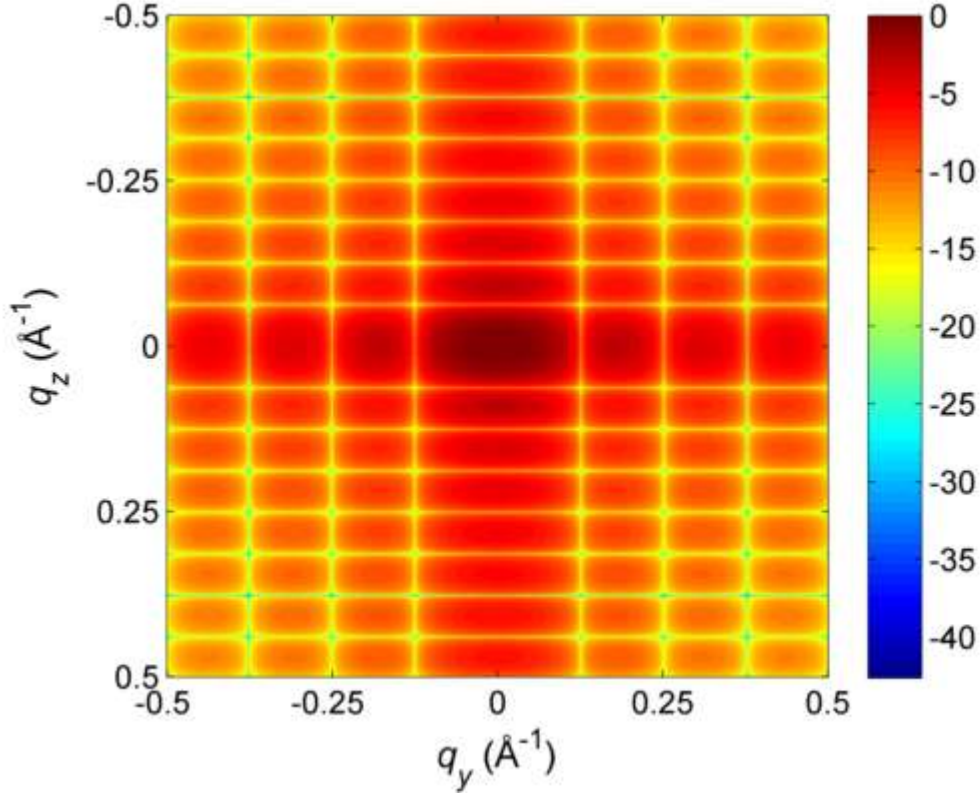


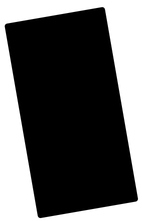
Polydispersity

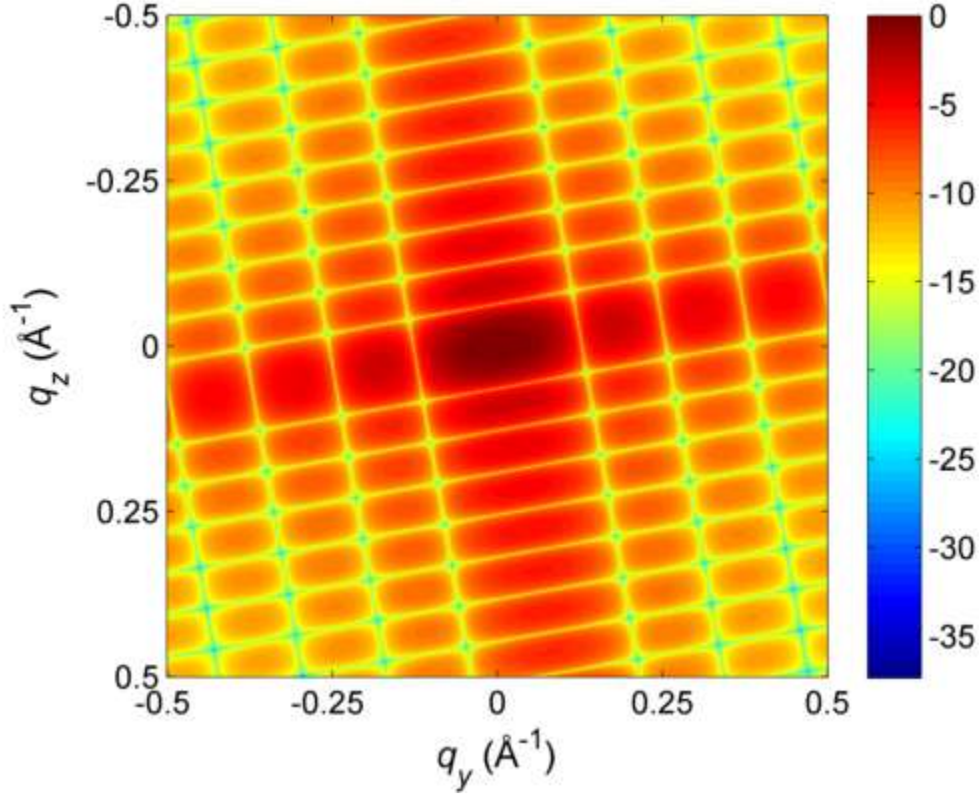


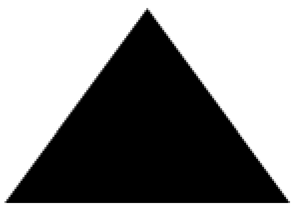


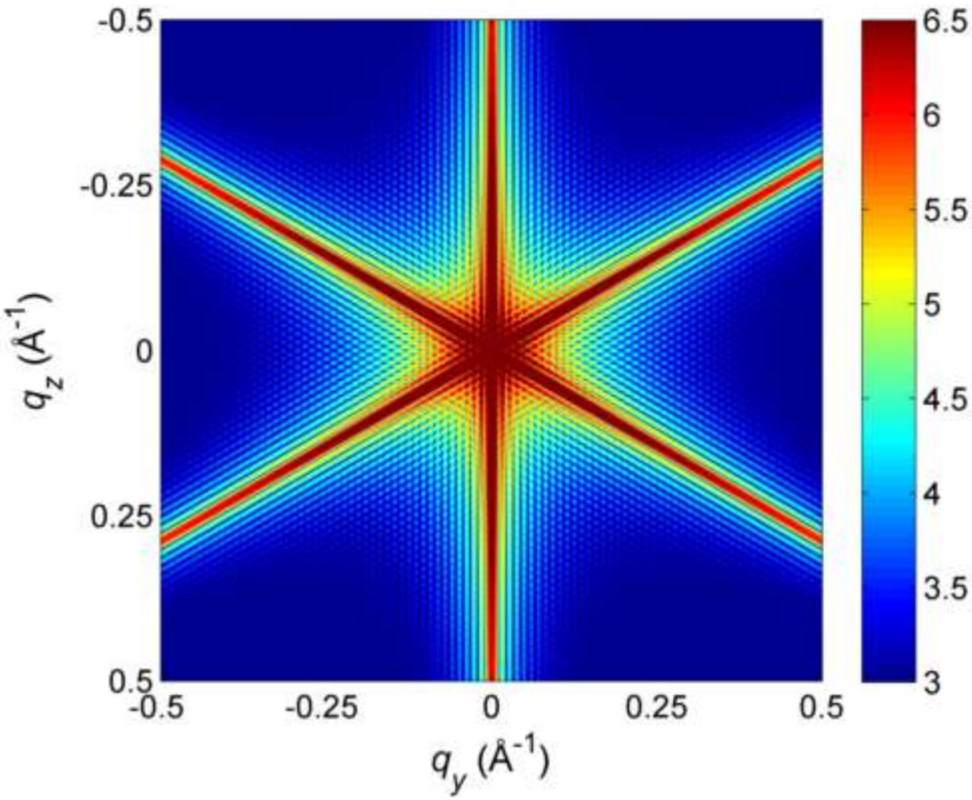
1. Scattering from a flat surface
2. Particle shape


-0.5
-0.25
0
0.25
0.5
q_z (Å^{-1})
-0.5
-0.25
0
0.25
0.5
q_y (Å^{-1})
0
-5
-10
-15
-20
-25
-30
-35
-40

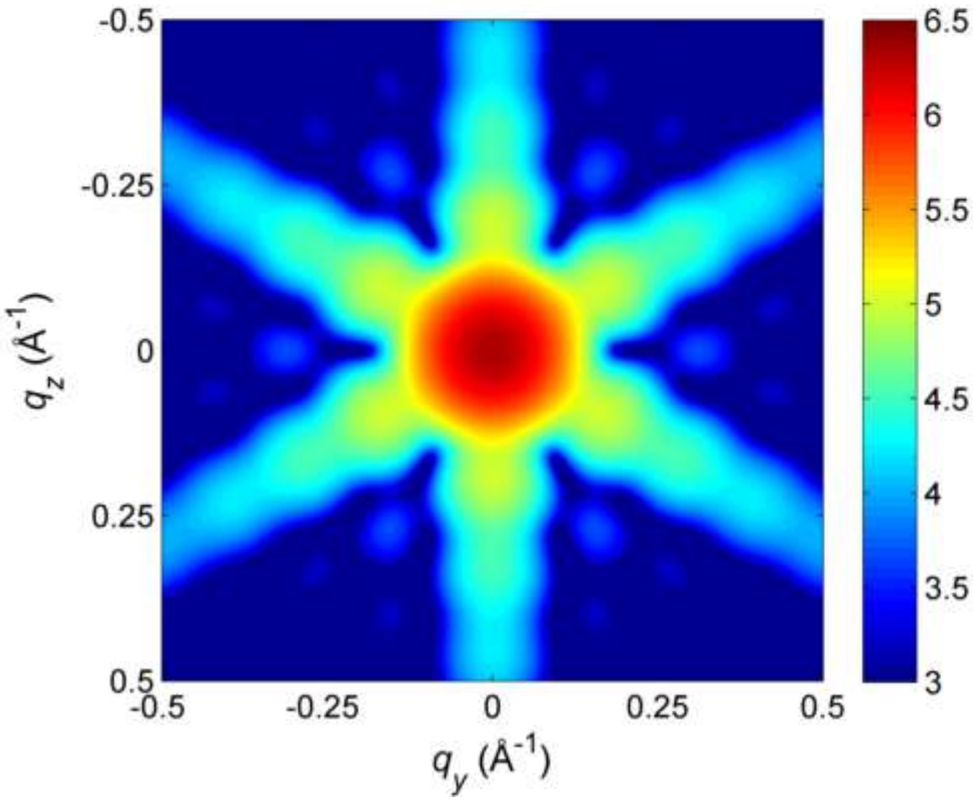


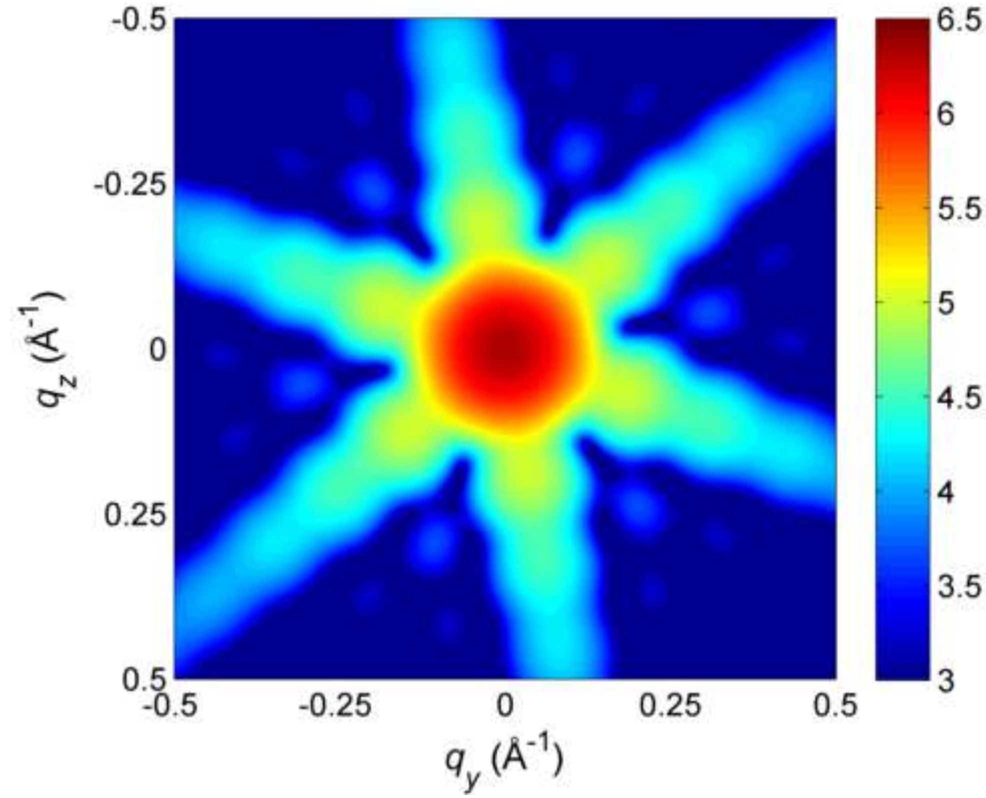

-0.5
-0.25
0
0.25
0.5
-0.5
-0.25
0
0.25
0.5
q_z (Å^{-1})
q_y (Å^{-1})
0
-5
-10
-15
-20
-25
-30
-35



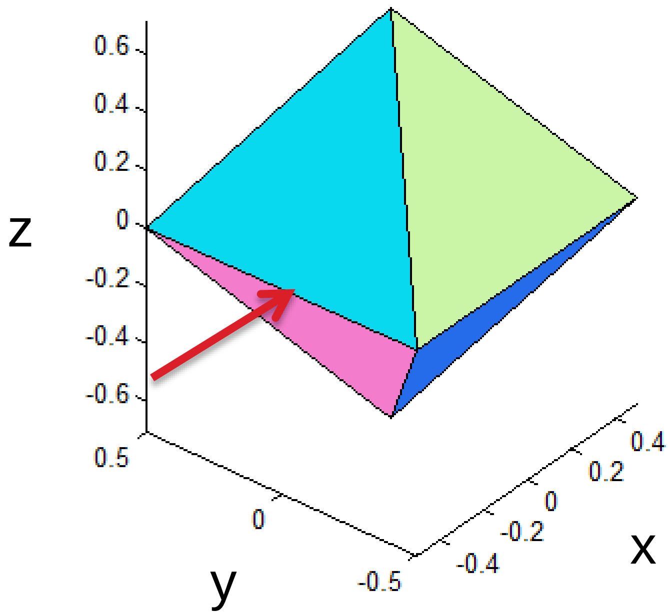


-0.5
-0.25
0
0.25
0.5
-0.5
-0.25
0
0.25
0.5
q_z (Å^{-1})
q_y (Å^{-1})
6.5
6
5.5
5
4.5
4
3.5
3

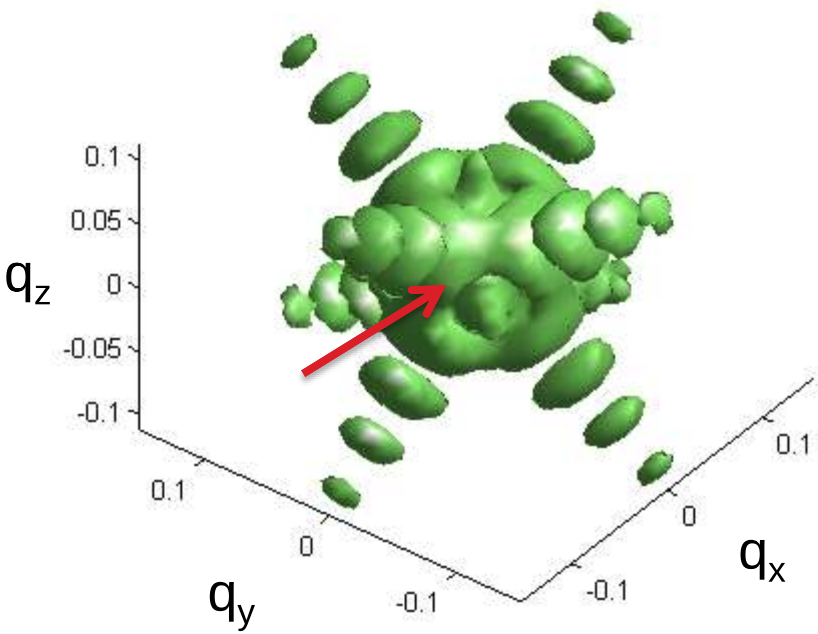

-0.5
-0.25
0
0.25
0.5
-0.5
-0.25
0
0.25
0.5
q_z (Å^{-1})
q_y (Å^{-1})
6.5
6
5.5
5
4.5
4
3.5
3


-0.5
-0.25
0
0.25
0.5
-0.5
-0.25
0
0.25
0.5
q_z (Å^-1)
q_y (Å^-1)
6.5
6
5.5
5
4.5
4
3.5
3

Octahedron

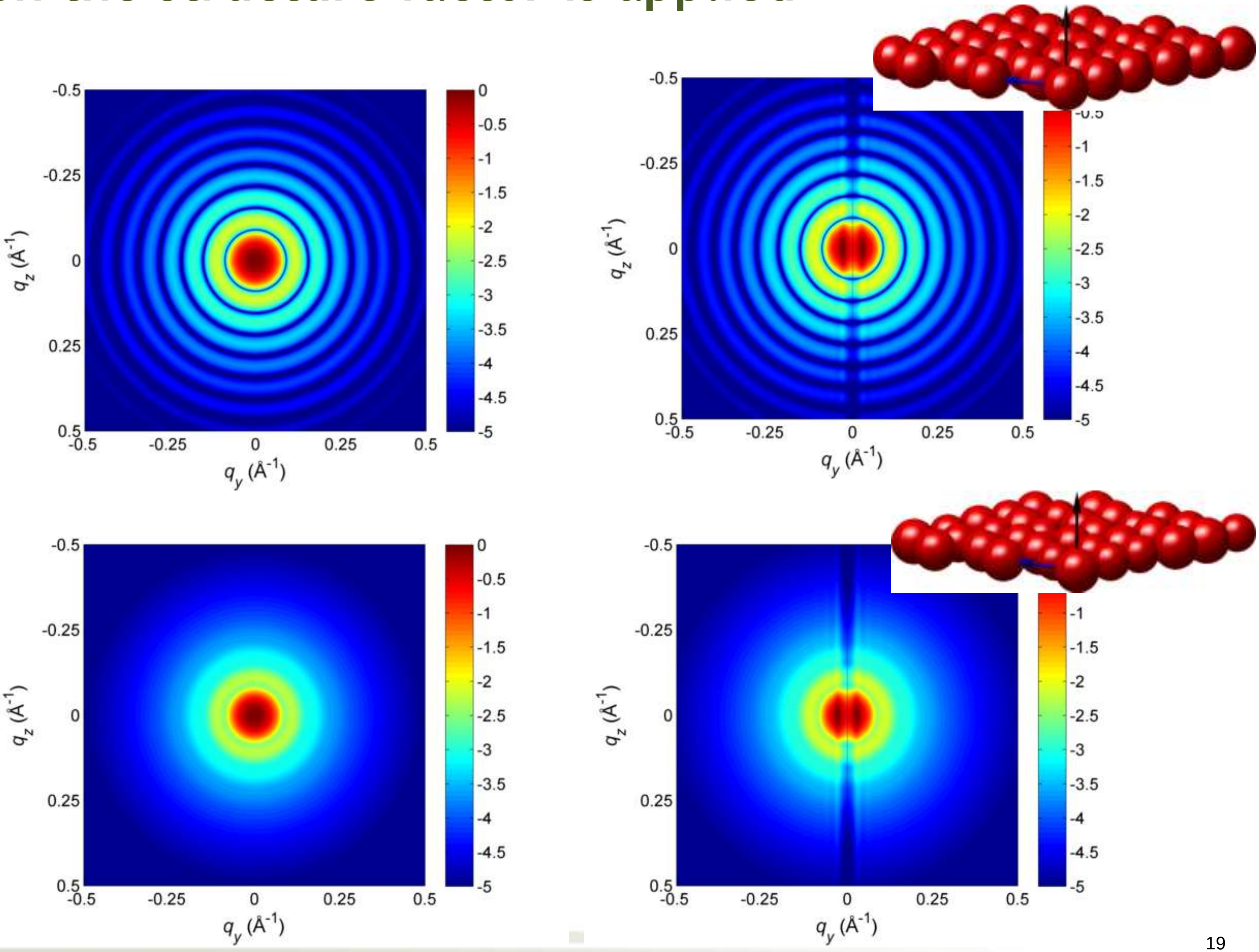


Real space

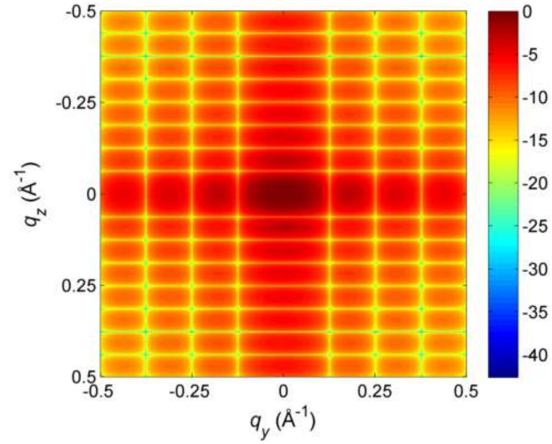


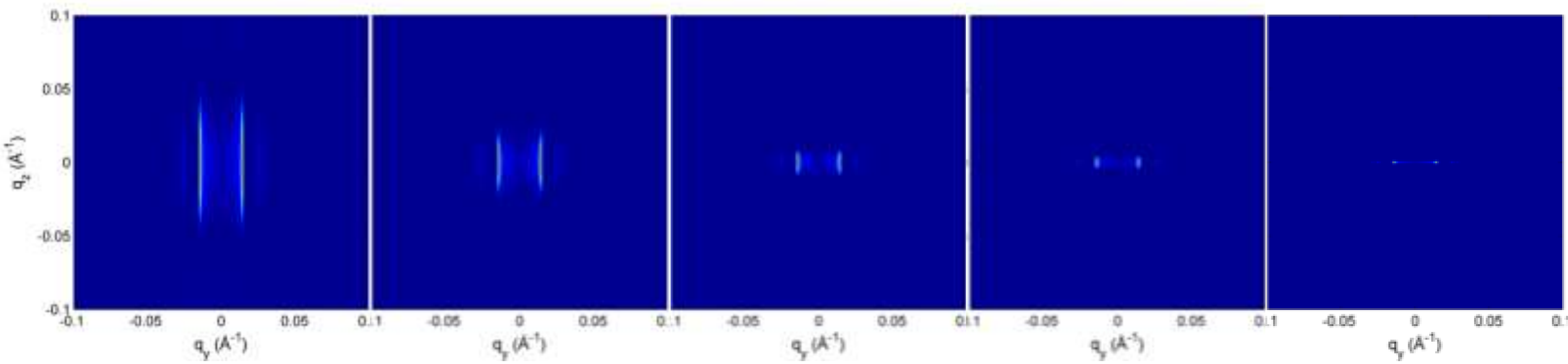
Reciprocal space

When the structure factor is applied



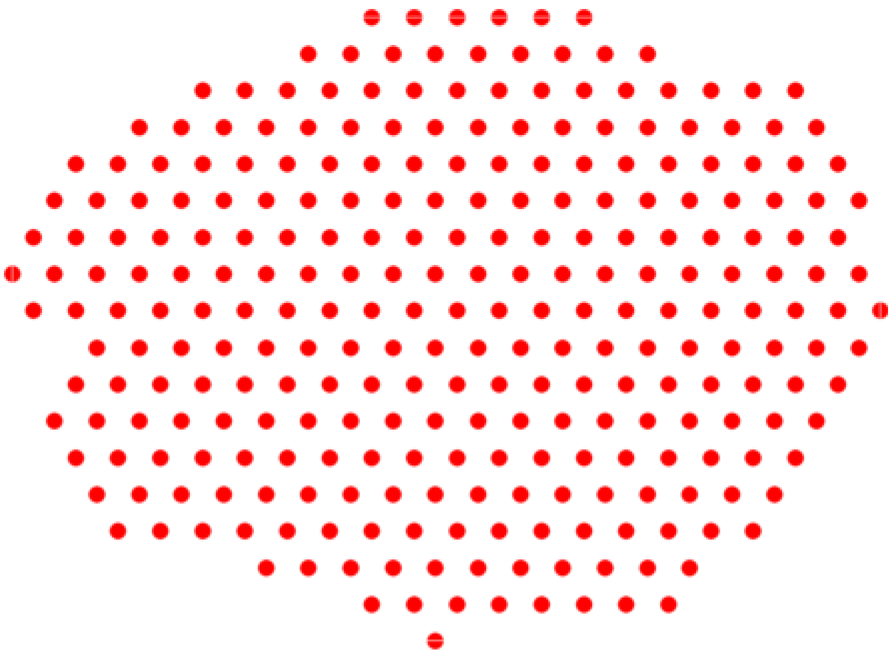
2D cylinders

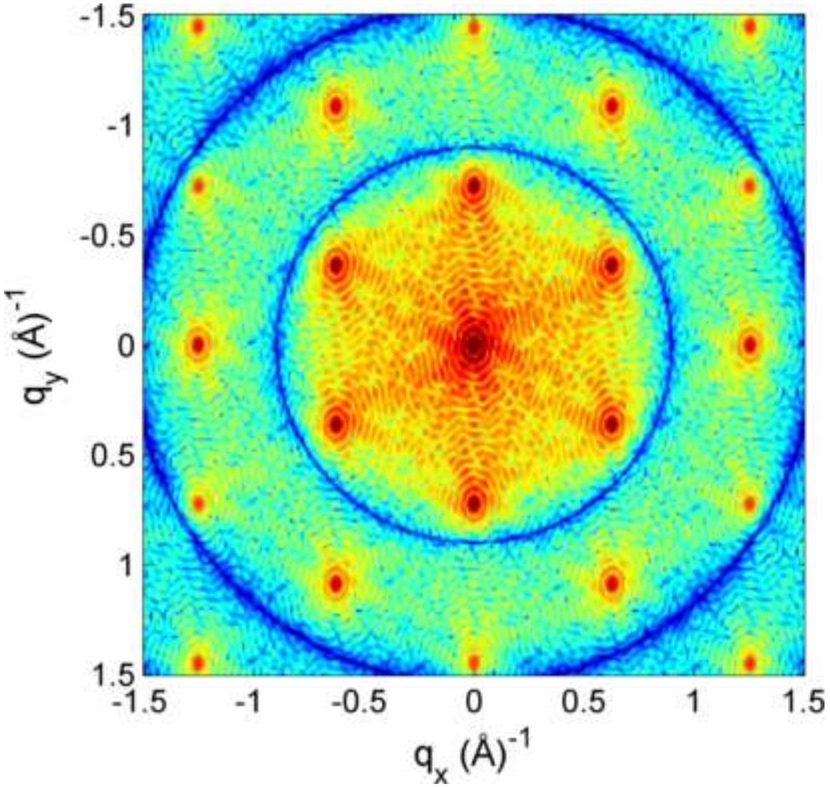


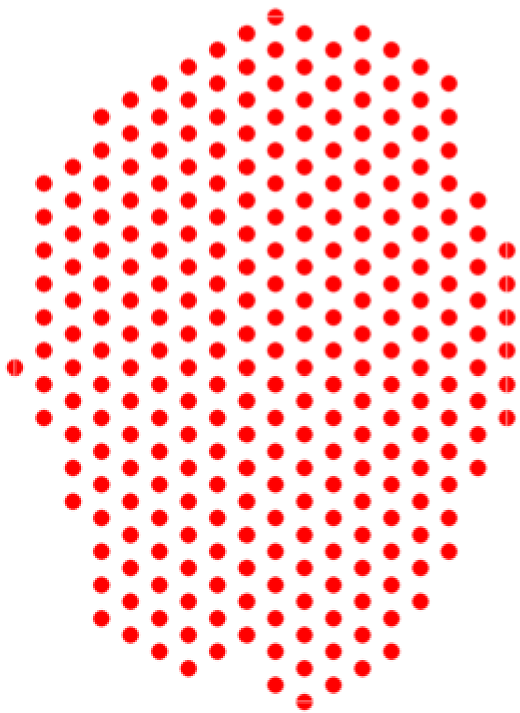


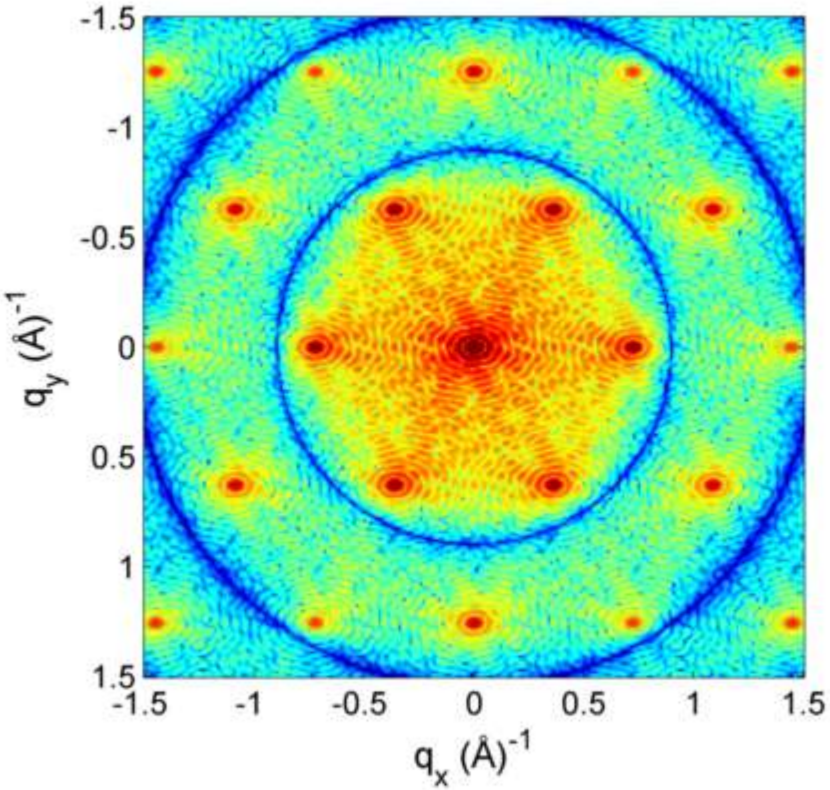
Height 10nm 20nm 50nm 100nm 500nm

lattices








-1.5
-1
-0.5
0
0.5
1
1.5
q_y (Å)$^{-1}$
-1.5
-1
-0.5
0
0.5
1
1.5
q_x (Å)$^{-1}$

Note

- So far, the intensities have been calculated NUMERICALLY
  - $I(\boldsymbol{q}) = \left|\sum_{i=1}^{N} F_i(\boldsymbol{q})\right|^2$
  - Takes a long time to model and calculate.

- Analytical ways will follow

How to split the form factor and the structure factor

- $I(\boldsymbol{q}) = \left|\sum_{i=1}^{N} F_i(\boldsymbol{q})\right|^2 = P(\boldsymbol{q})S(\boldsymbol{q})$

- Decoupling approximation (DA)

- Local Monodisperse Approximation (LMA)

The form factor

$$F(\boldsymbol{q}) = \rho \int_V e^{-j\boldsymbol{q}\cdot\boldsymbol{r}} d\boldsymbol{r}$$

$$\begin{aligned} P(q) &= \langle \overline{|F(q)|^2} \rangle \\ &= \sum_{l=1}^{N_p} \frac{N_l}{N_p} \langle |F_l(q)|^2 \rangle \\ &= \int n(r) \langle |F_l(q)|^2 \rangle dr \end{aligned}$$

The form factor models from Babonneau's software

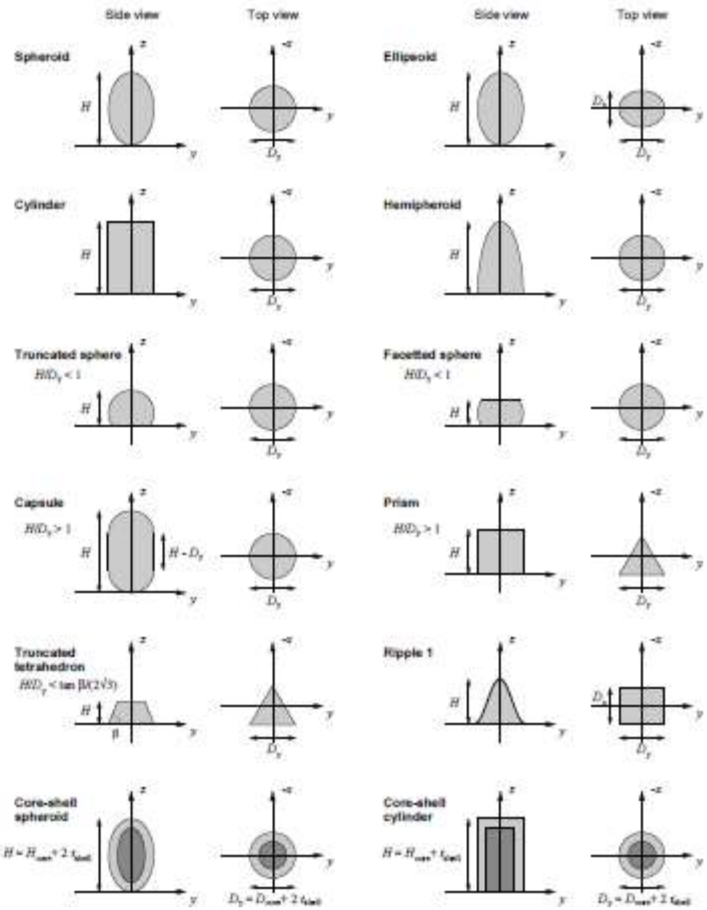


FIGURE 3 – Form factors included in the FitGISAXS package.

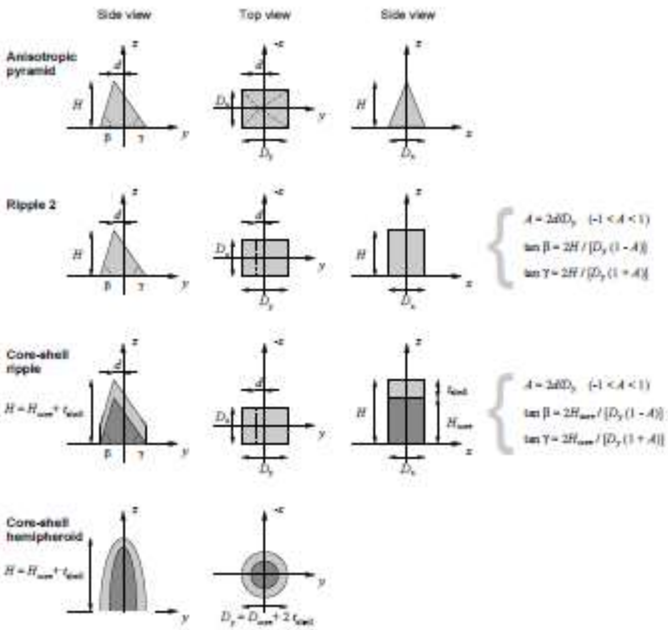
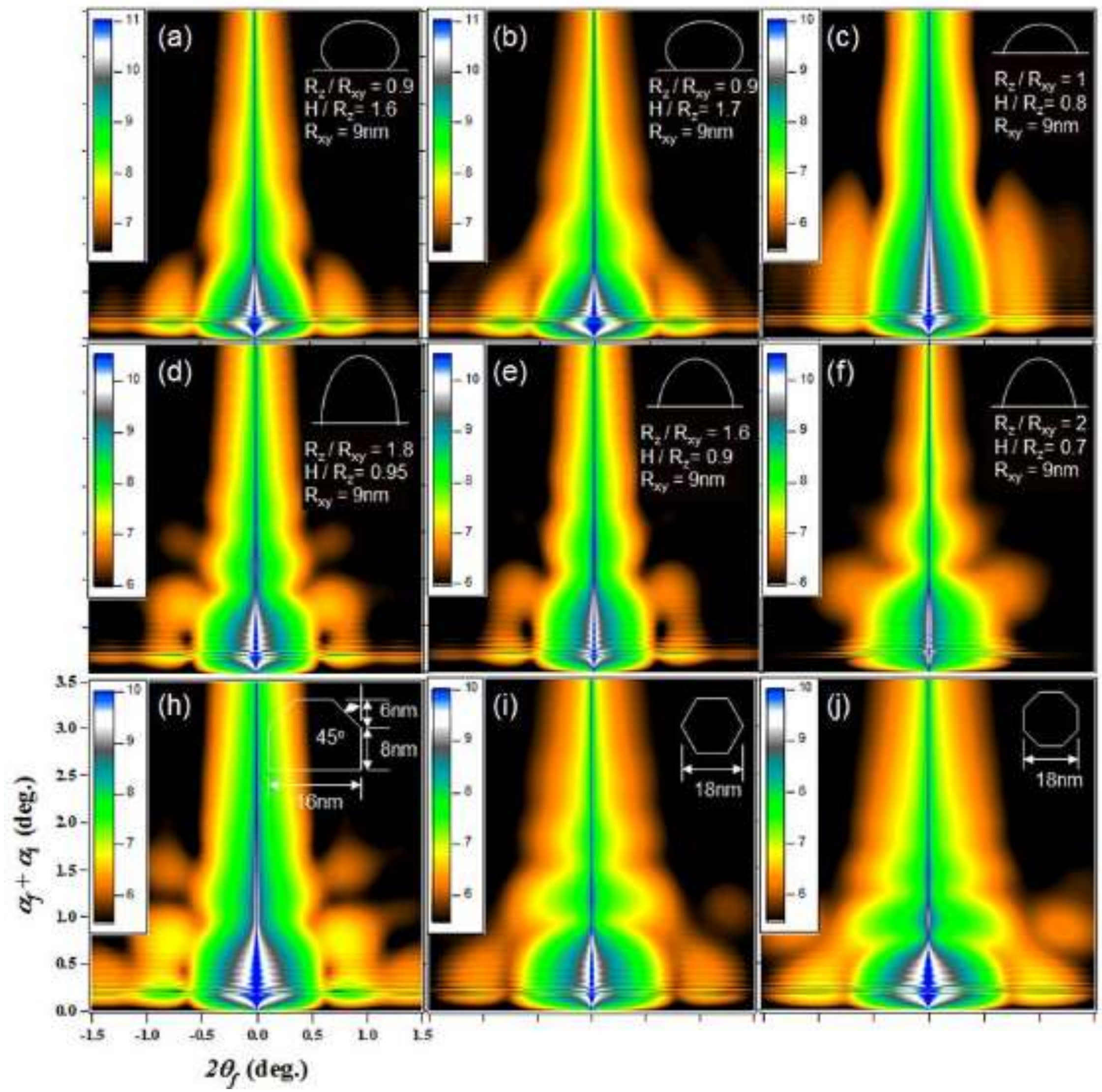


FIGURE 4 – Additional form factors included in the FitGISAXS package.

Rods laid down on a substrate



B. Lee et al. Langmuir, 2007, 23 (22), pp 11157–11163

The size distribution model

- Gaussian
- Double Gaussian for the bimodal distribution.
- Log-normal
- Double Log-normal for the bimodal distribution.
- Weibull
- Schultz-Zimm function

The structure factors from Babonneau’s software

- Random organization: S(q) = 1
- Percus-Yevick 3D : Hard sphere potential
- Percus-Yevick 2D

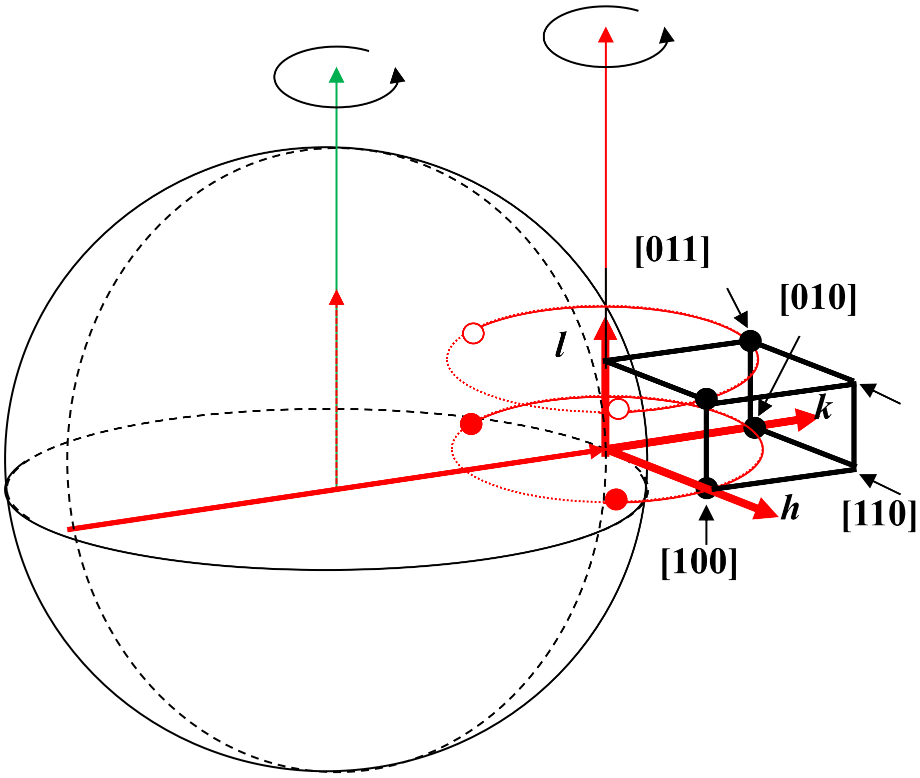
- Paracrystal 1D
- Paracrystal 2D rectangular
- Paracrystal 2D hexagonal

- And many others.. See IsGISAXS manuals.

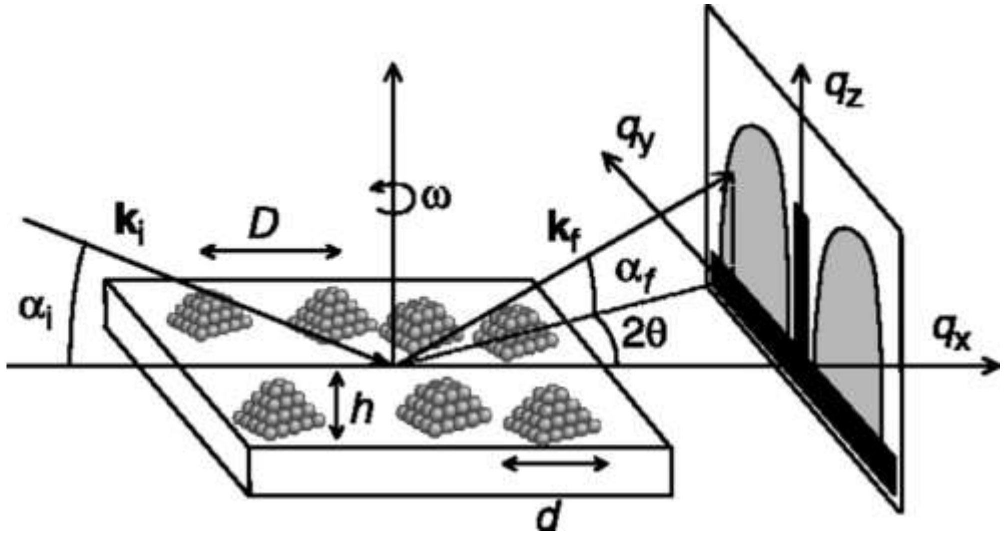
Reciprocal space or scattering vector q

- The scattering vector q is not a scalar but a vector. (qx, qy, qz)
- When a lattice (or a sample) rotate, the reciprocal lattice (or the scattering from the sample) rotates.
- The Bragg condition is not only q = 2*pi/d .

Ewald sphere



Definitions of angles and the q space

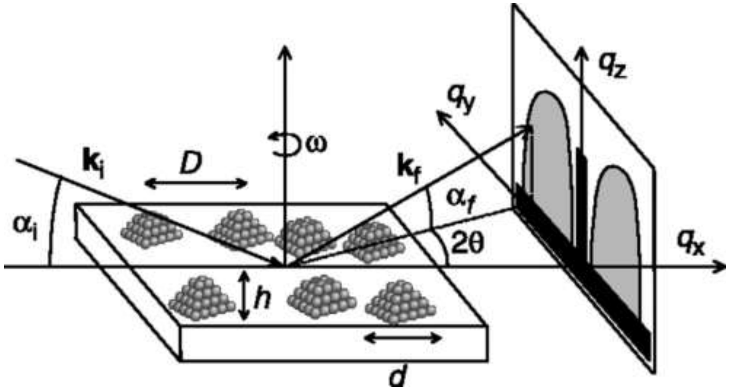


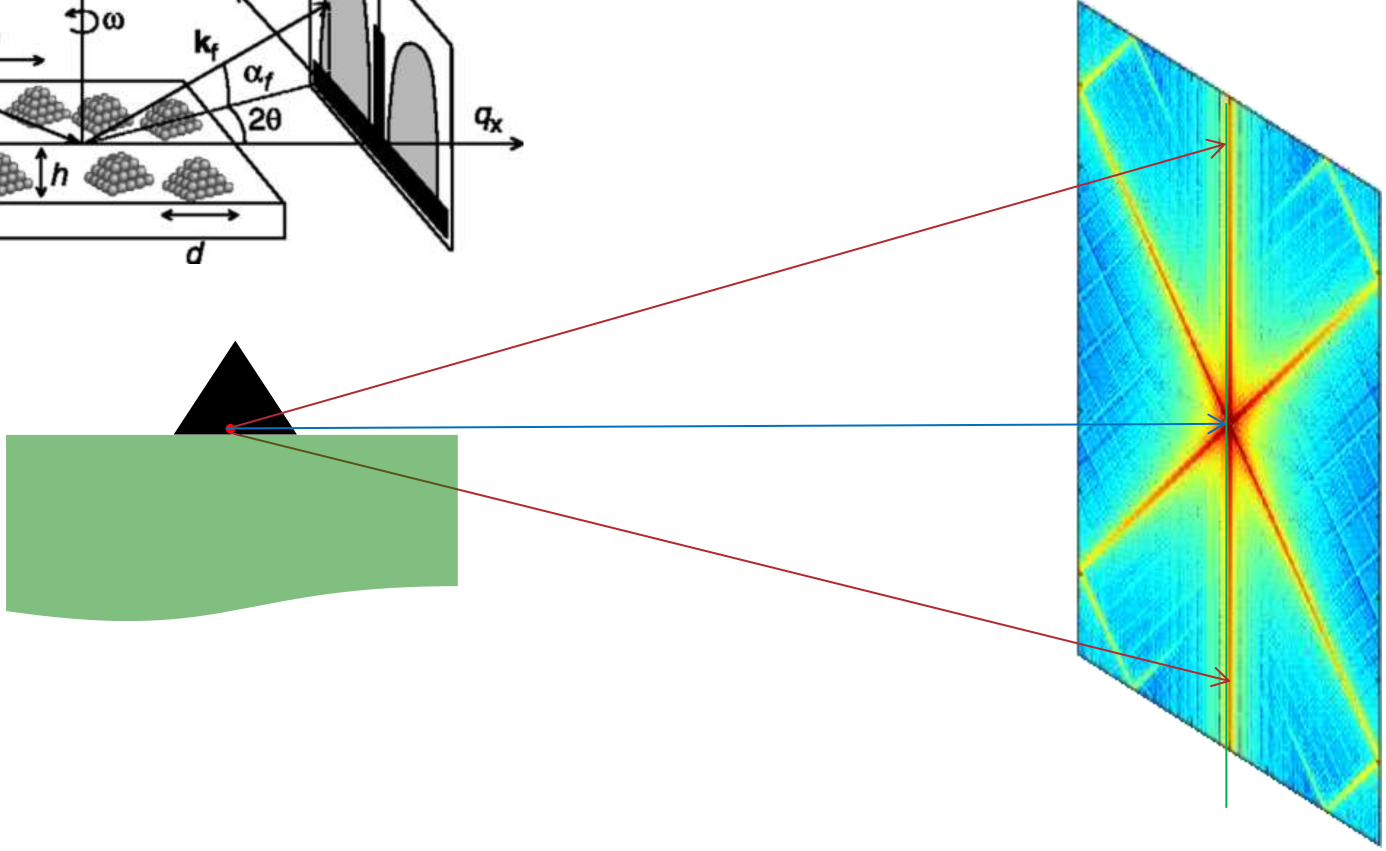
Note

- Effects due to the grazing incidence geometry
  - Absorption
  - Reflection
  - Refraction

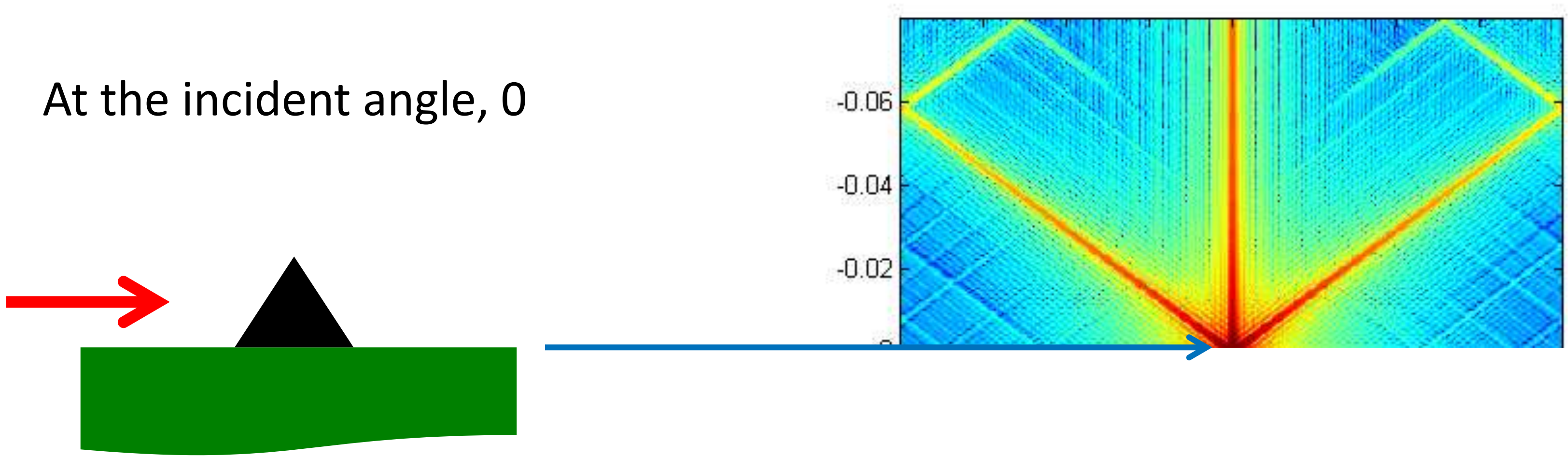
- These effects are highly depending on the sample.
  - Supported island.
  - Buried particles.
  - Sandwiched particles.
  - …

In GISAXS, you can measure only the upper half
- Substrate absorbs the downward scattering

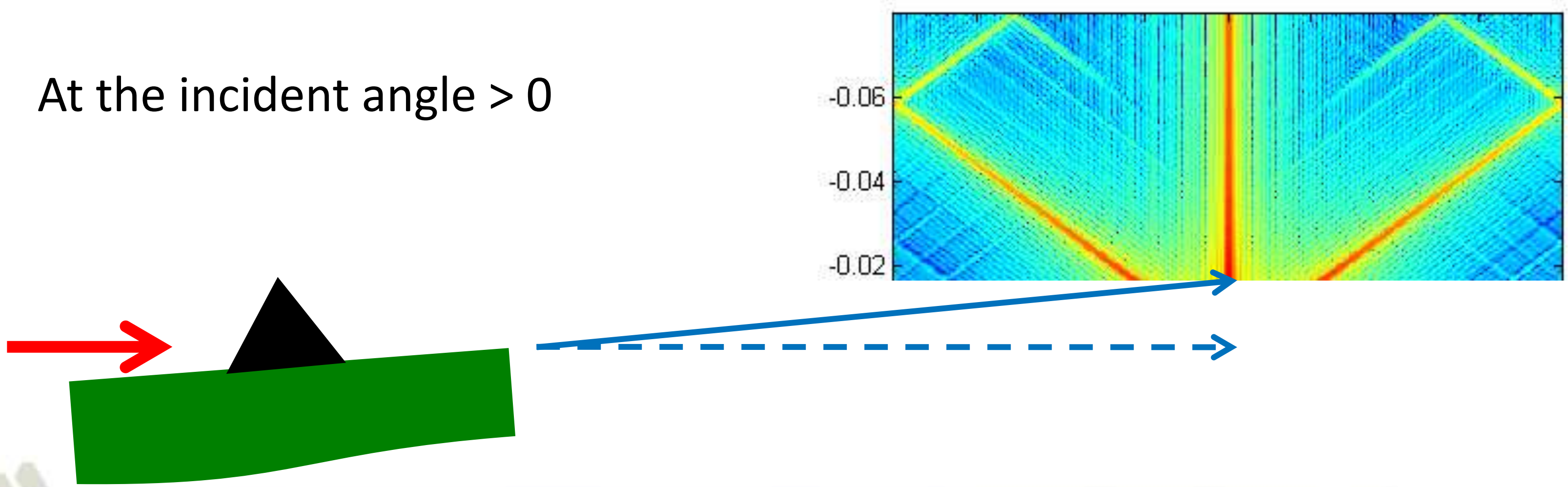




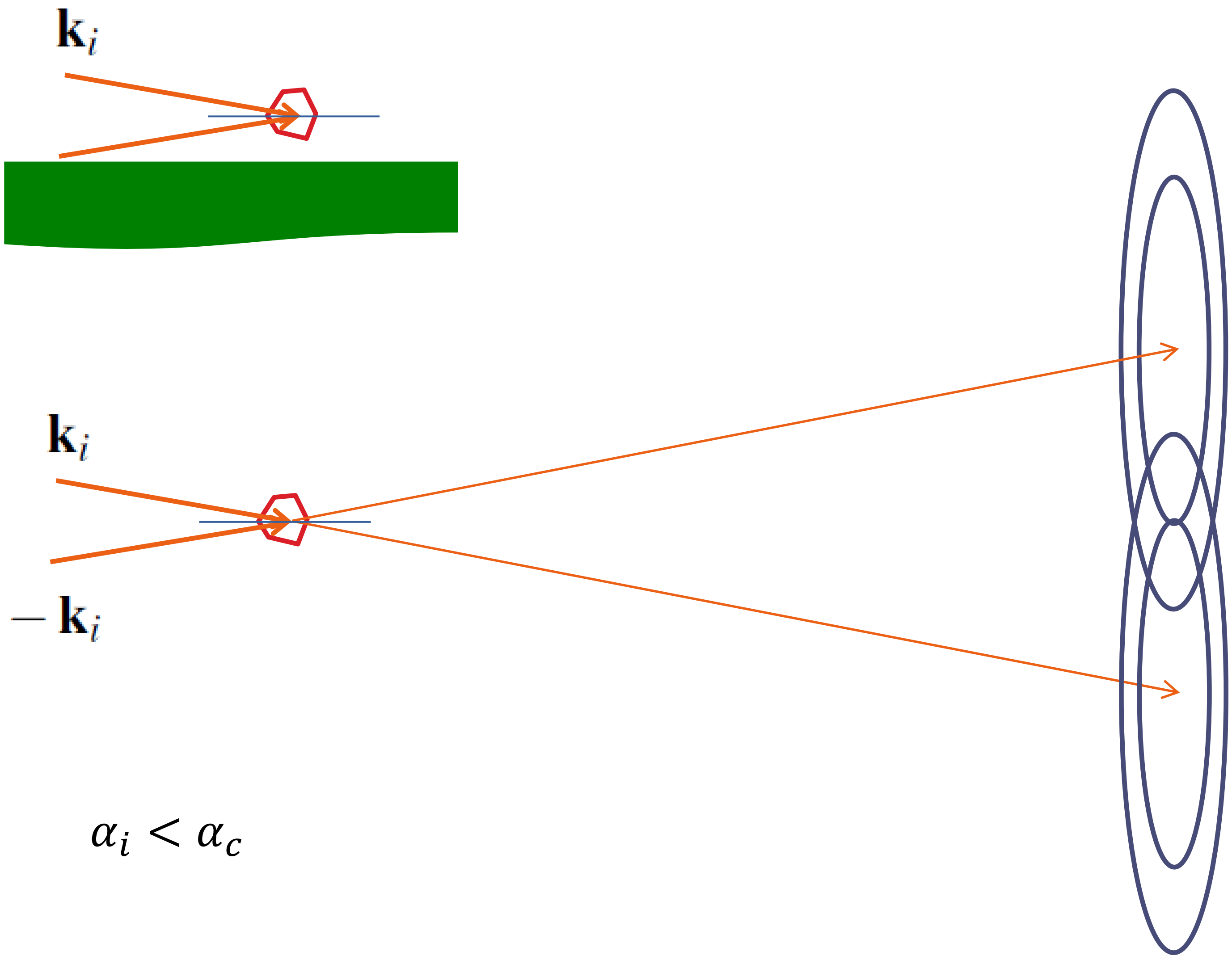
At the incident angle, 0



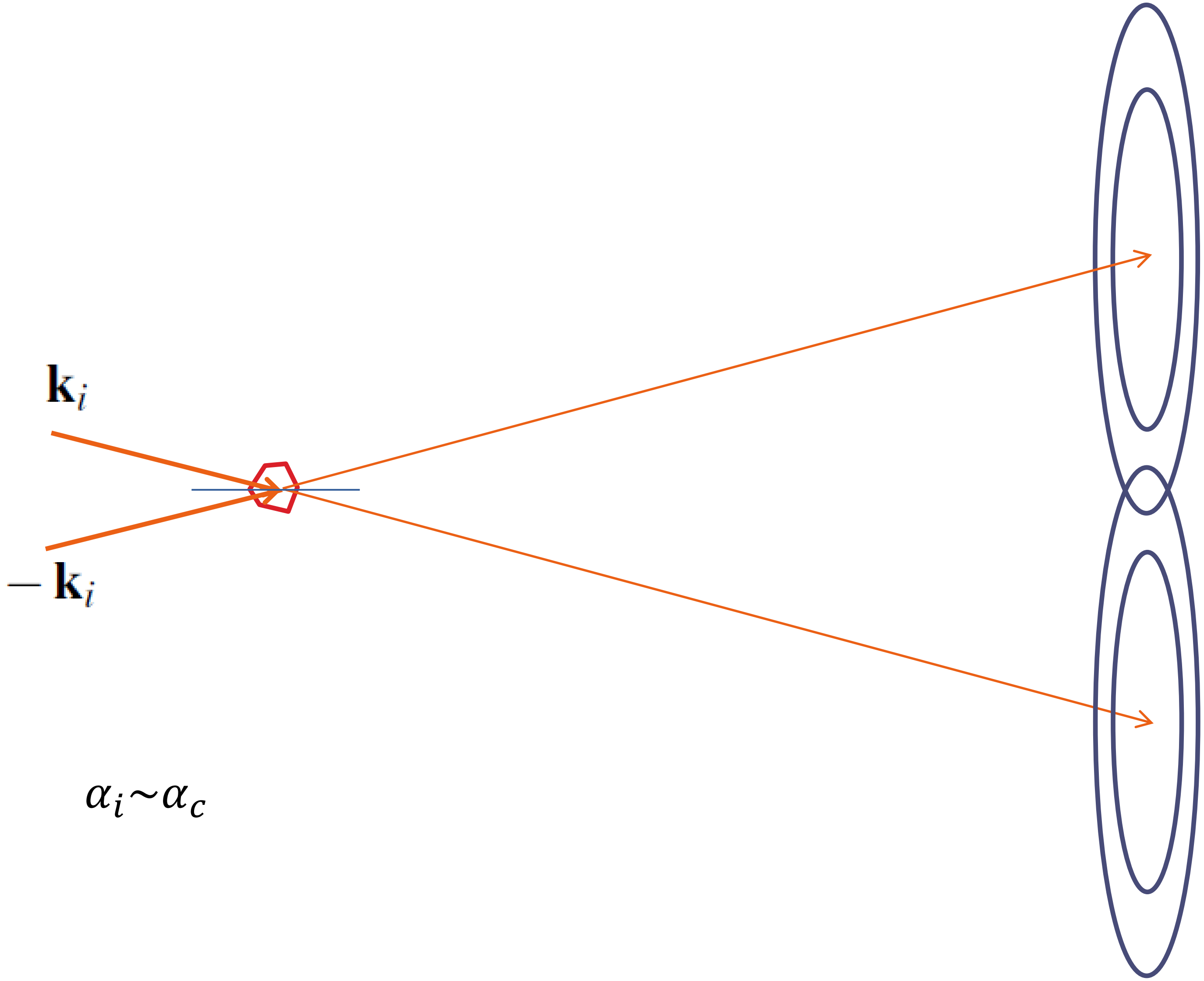
At the incident angle > 0



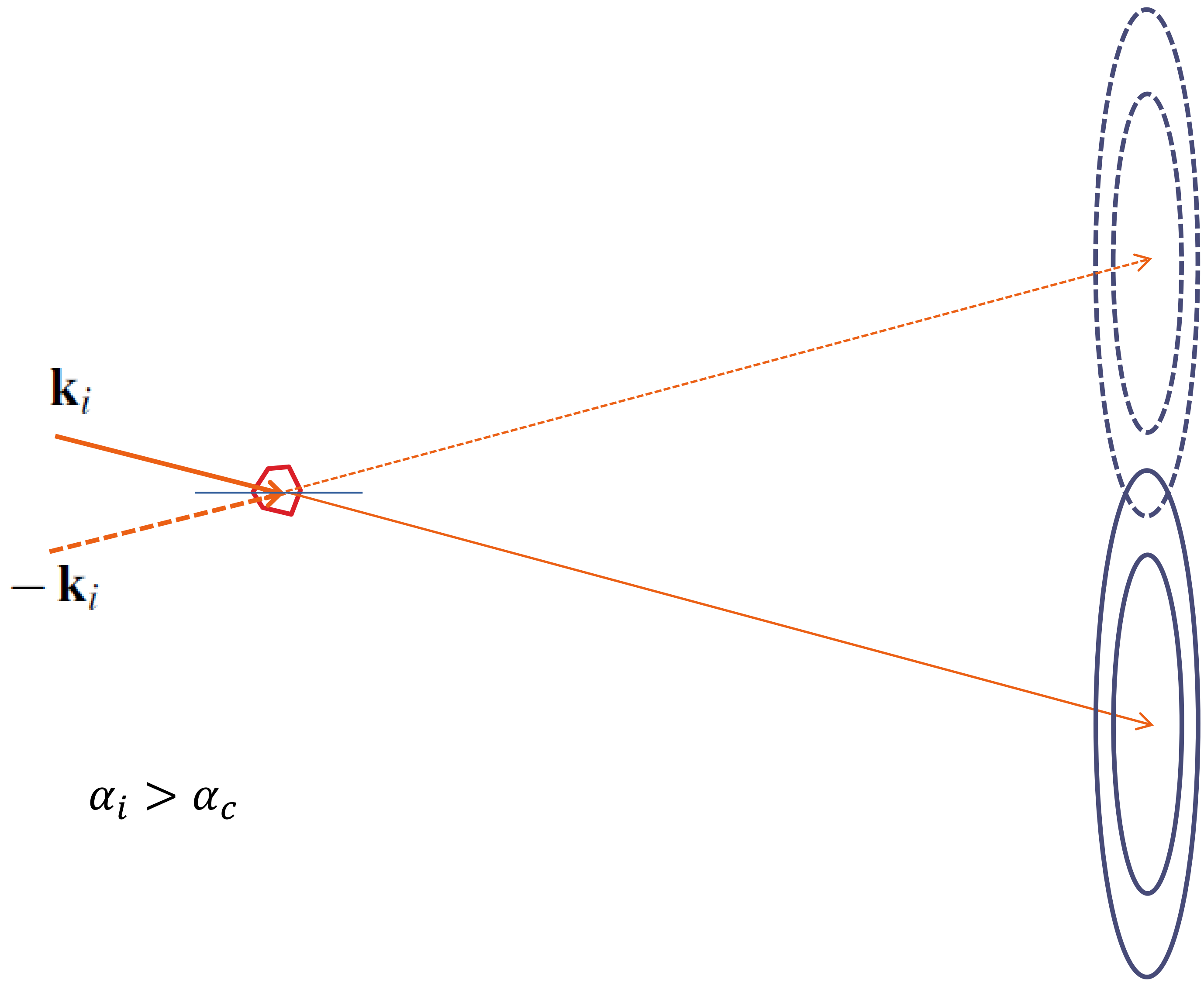
The effect of a small incident angle
1. Reflection causes an additional incident beam

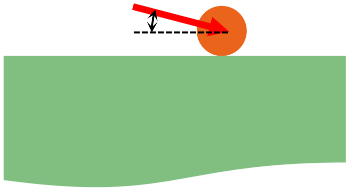


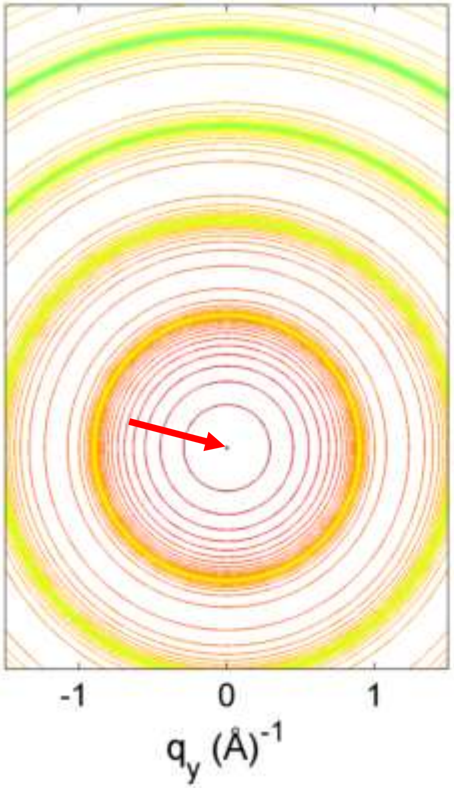
$\alpha_i < \alpha_c$

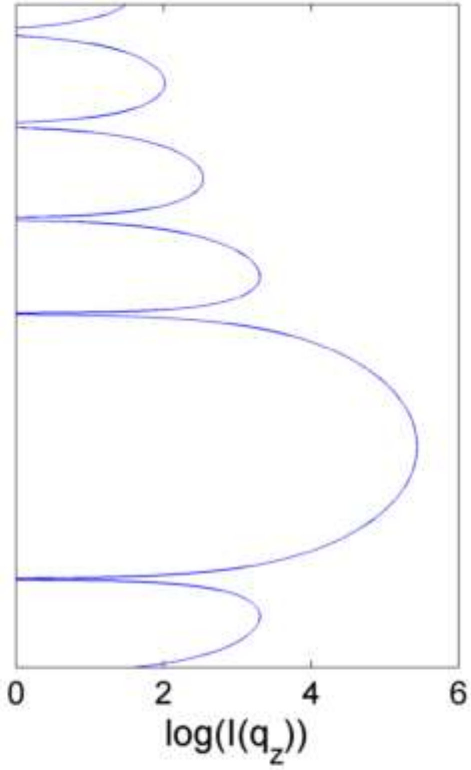


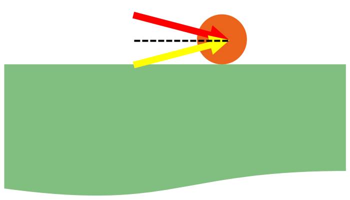
$\alpha_i \sim \alpha_c$

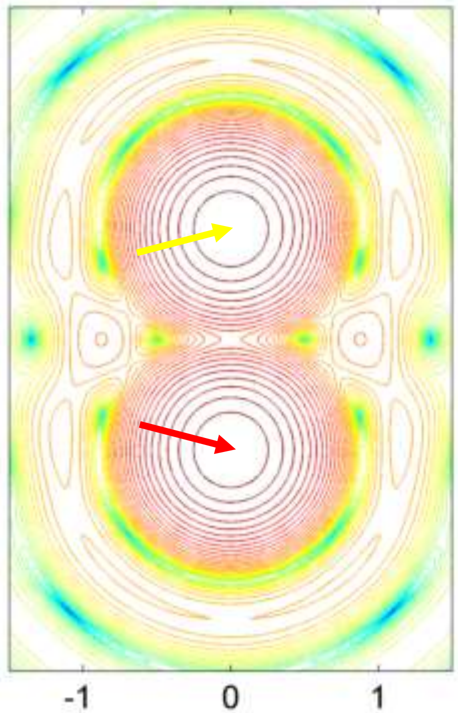

$\mathbf{k}_i$
$-\mathbf{k}_i$
$\alpha_i > \alpha_c$

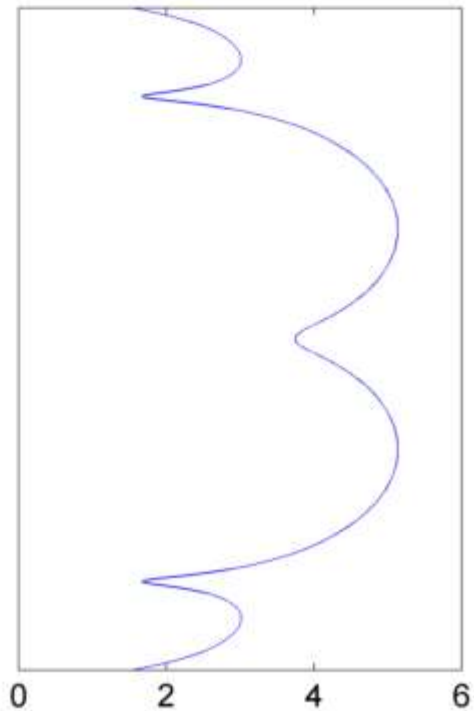


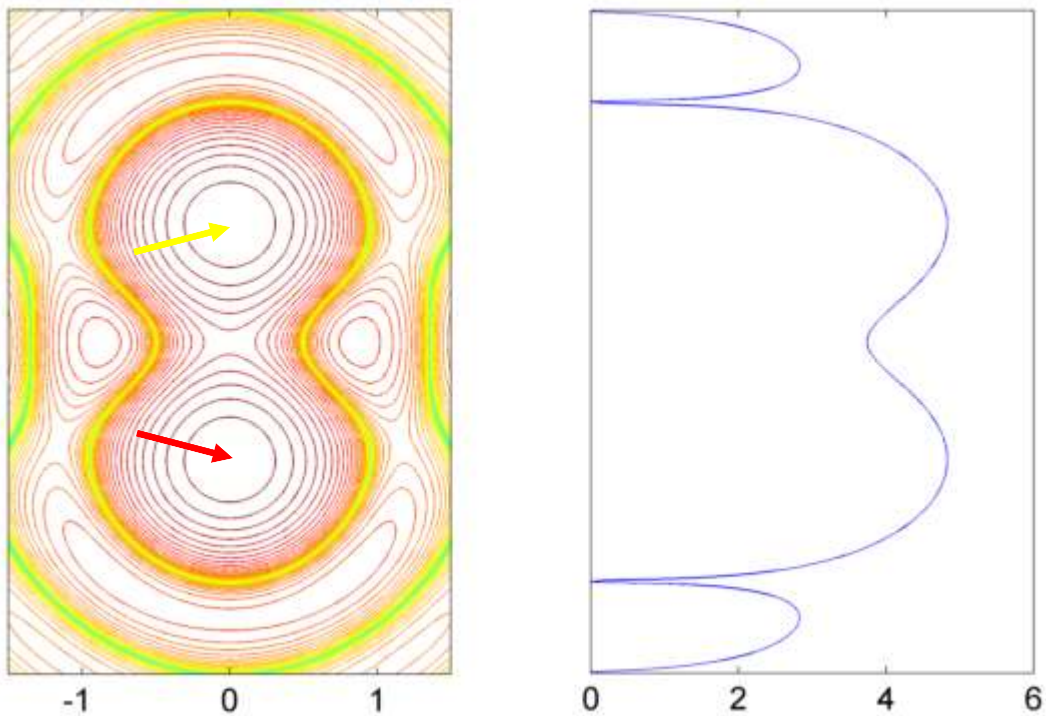

-1
0
1
q_y (Å)$^{-1}$


0
2
4
6
log(I(q_z))

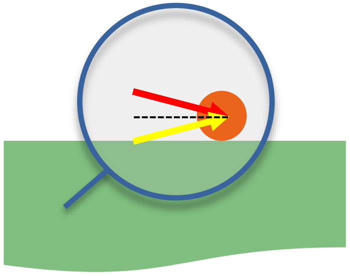


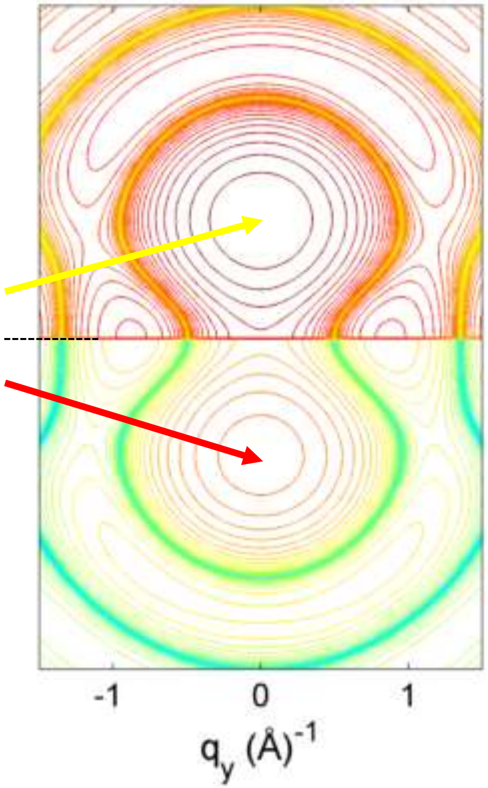

-1
0
1


0
2
4
6

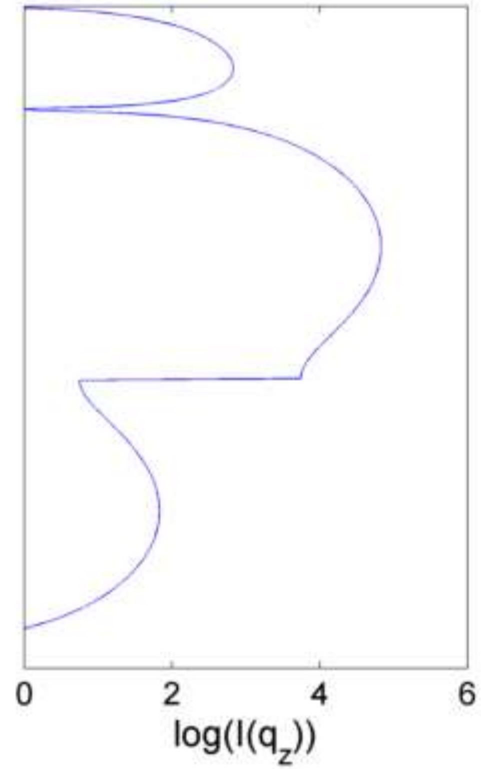


-1
0
1
0
2
4
6



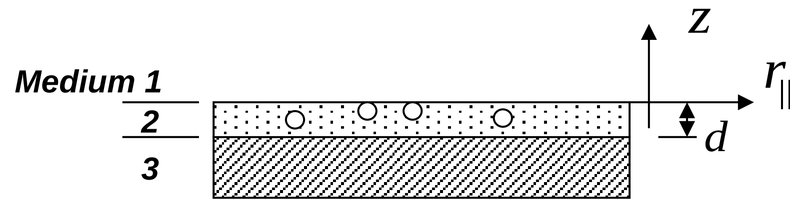


-1
0
1
q_y (Å)$^{-1}$

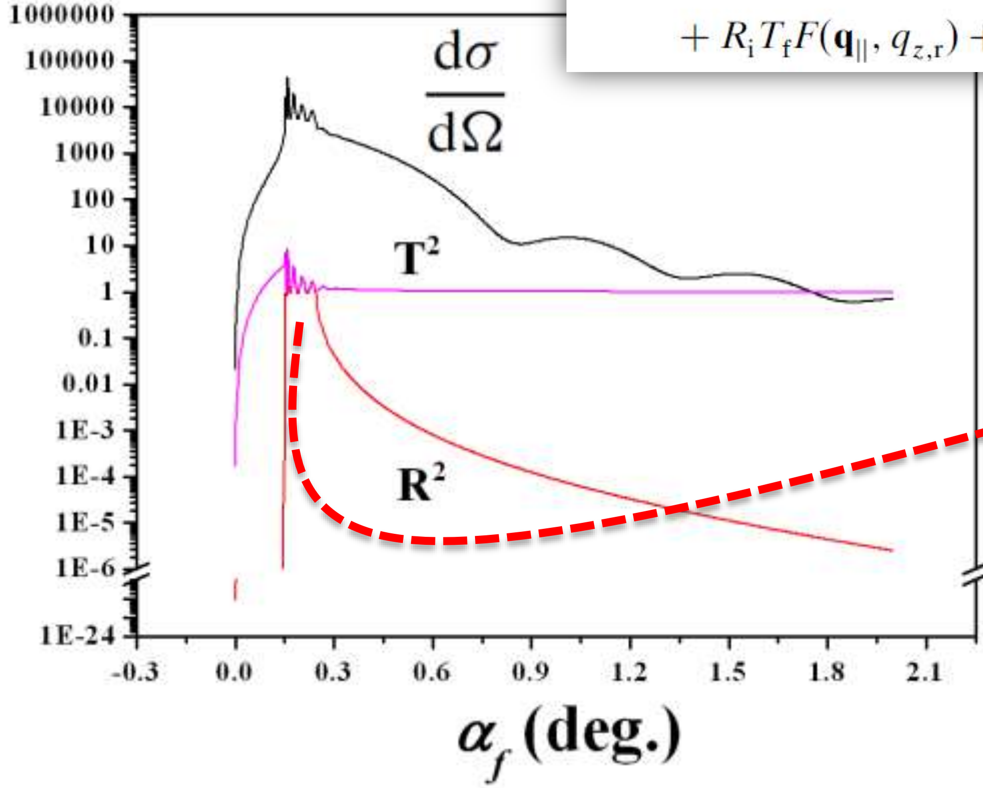


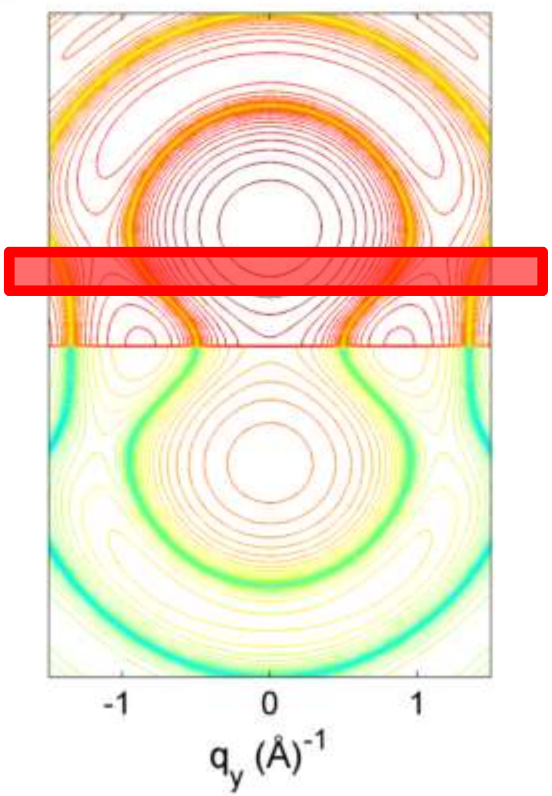
0
2
4
6
$\log(I(q_z))$

Effect of wave amplitudes

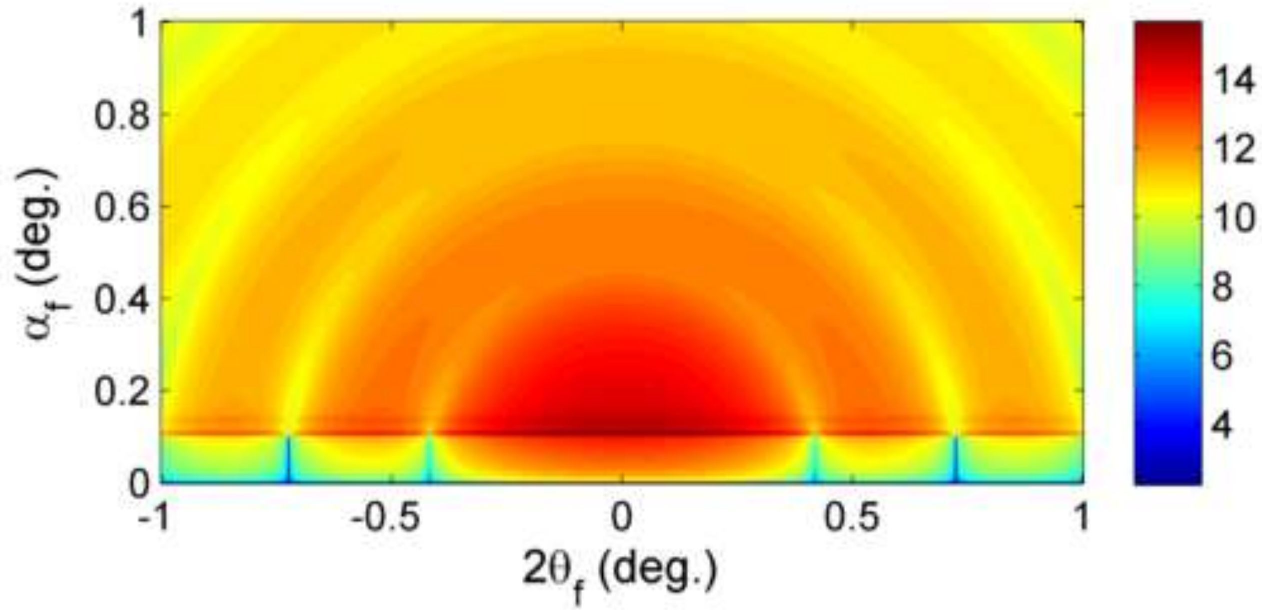


$$
\begin{aligned}
\frac{d\sigma}{d\Omega} &= r^2 \psi_{sc}(r)\psi^*_{sc}(r) \\
&= A\left| T_i T_f F(\mathbf{q}_{||}, q_{z,t}) + T_i R_f F(\mathbf{q}_{||}, -q_{z,r}) \right. \\
&\quad \left. + R_i T_f F(\mathbf{q}_{||}, q_{z,r}) + R_i R_f F(\mathbf{q}_{||}, -q_{z,t}) \right|^2
\end{aligned}
$$



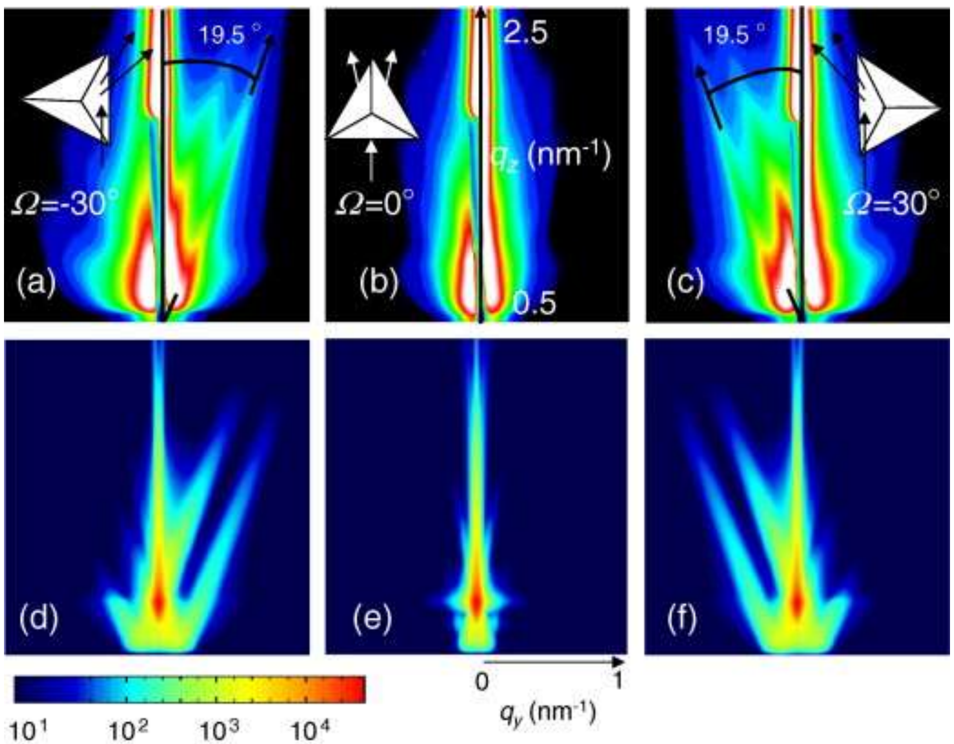


GISAXS from a sphere / log scale image

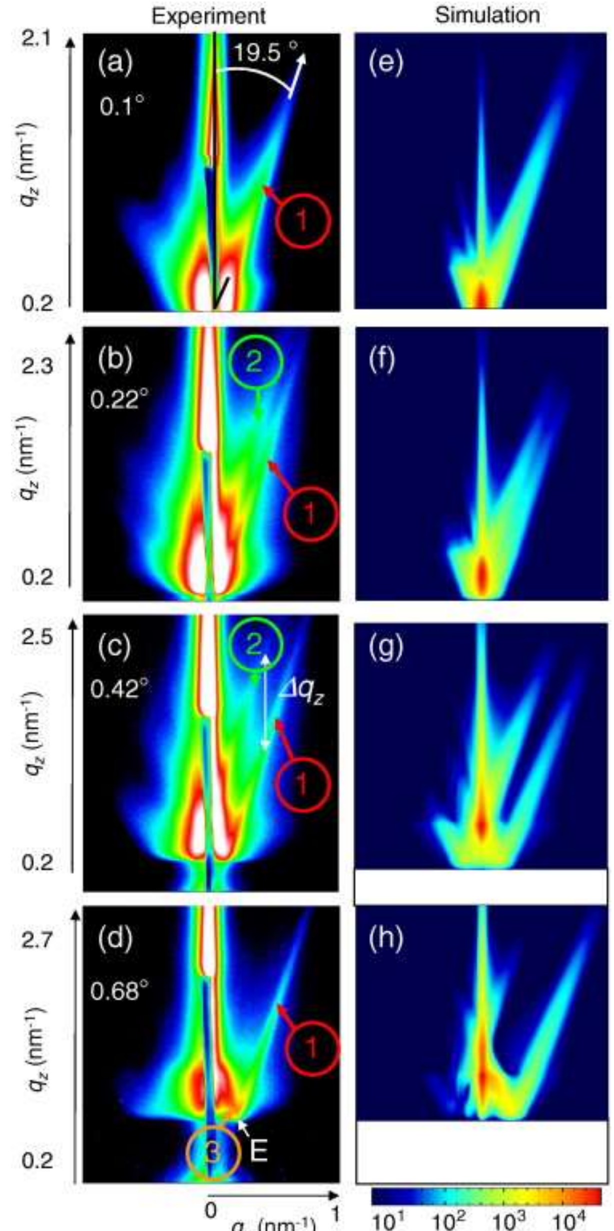


Example

A facetted Pt/W(211) sample annealed at 1340 K

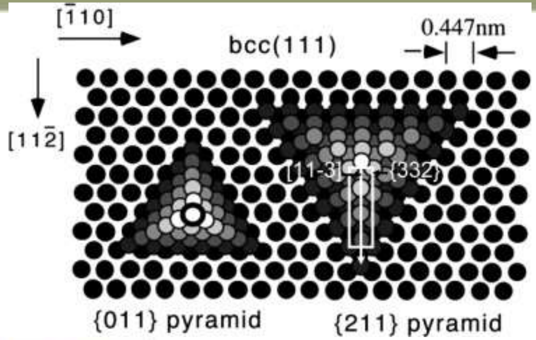


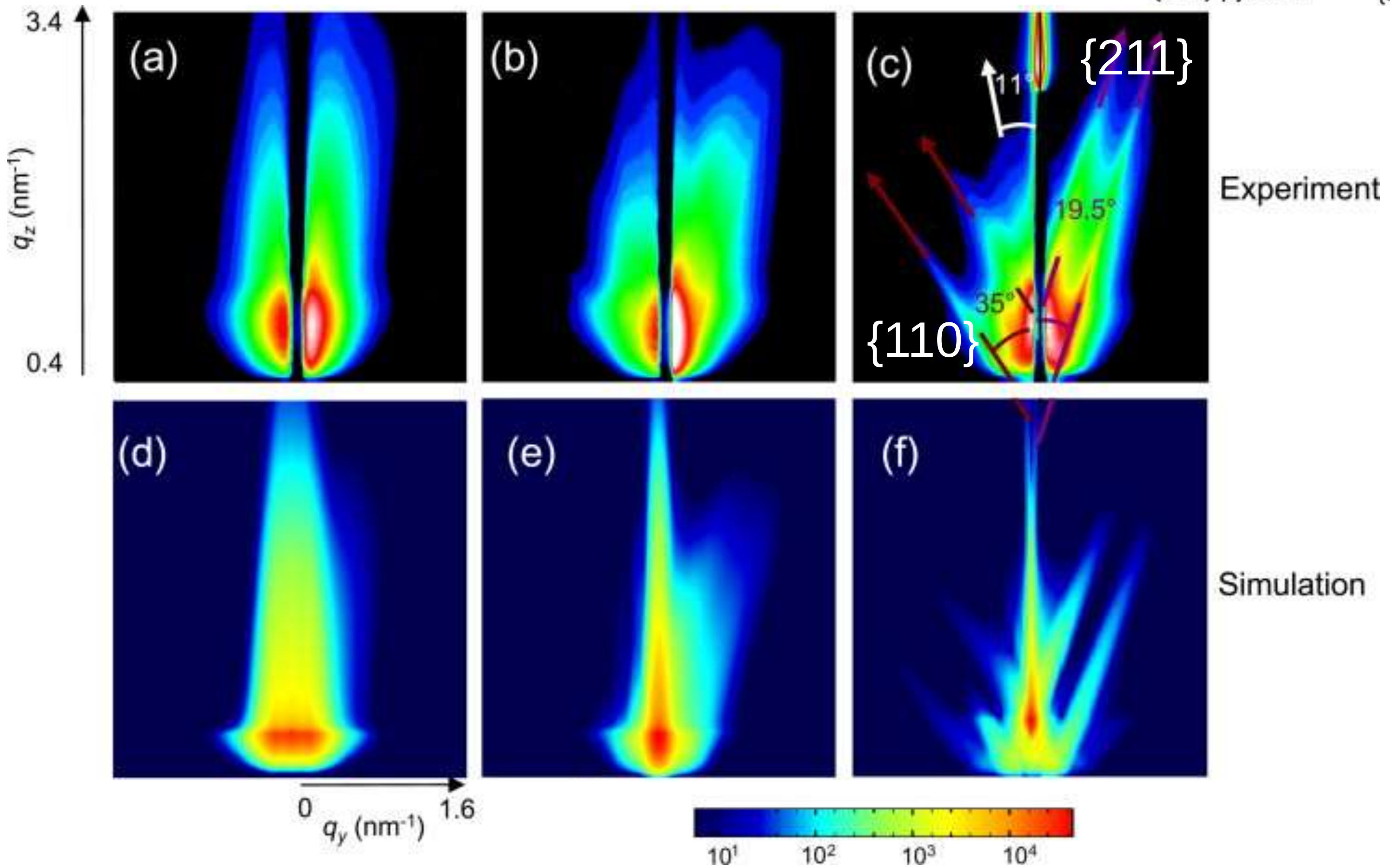
Measured at different azimuth angles



Measured at different incident angles: (a) 0.1°, (b) 0.22°, (c) 0.42°, (d) 0.68°.

C. Revenant *et al.*, Surface Science, 601, 16, 3431

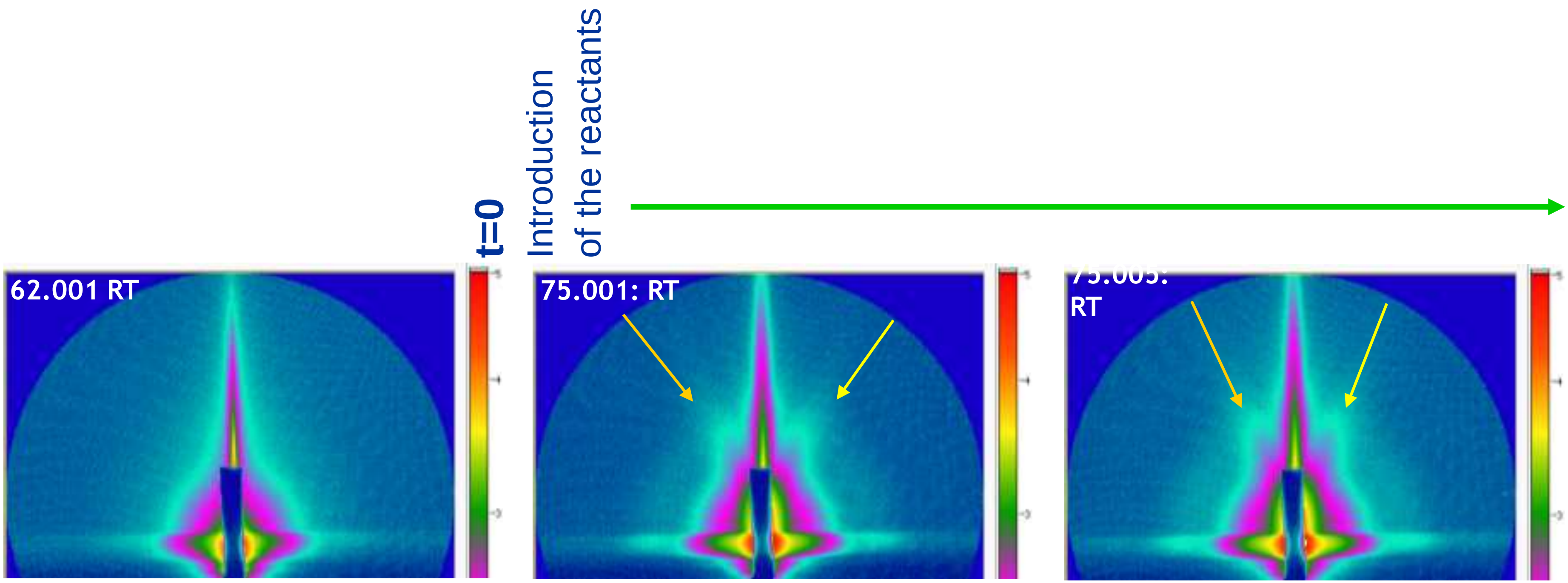




0.8 nm Co/1.1 ML Pt/W after an annealing during (a) 3 min at 920–1000 K, (b) 3 min at 1020–1100 K, (c) 3 min at 1140–1210 K. Respective simulated 2D GISAXS patterns from (d) to (f).

C. Revenant *et al.*, Surface Science, 601, 16, 3431

Shape changes with Ag nanoparticles in propylene epoxidation



- oblate particles
- flattening (decrease in height)
- wetting angle at the nanoparticle/ support interface resolved
- change of the wetting angle at nanoparticle/support interface with time at room temperature (indicated by arrows)

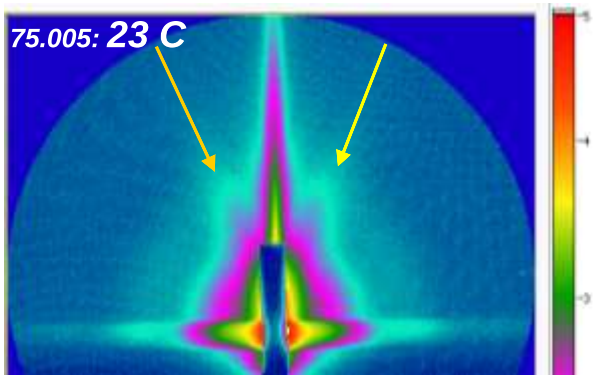
Under ~1 atm. pressure of 1.0% propylene and 0.5% oxygen in He

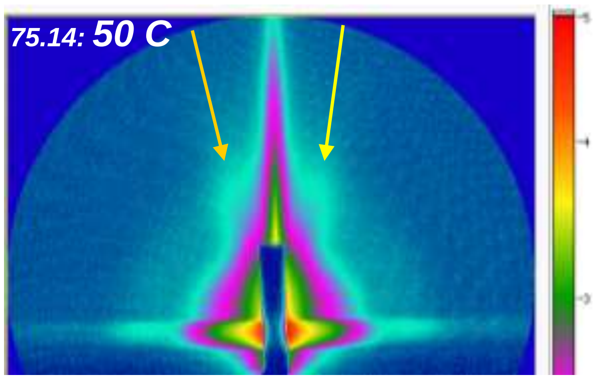
On 6 cycle Al_2O_3 over SiO_2/Si

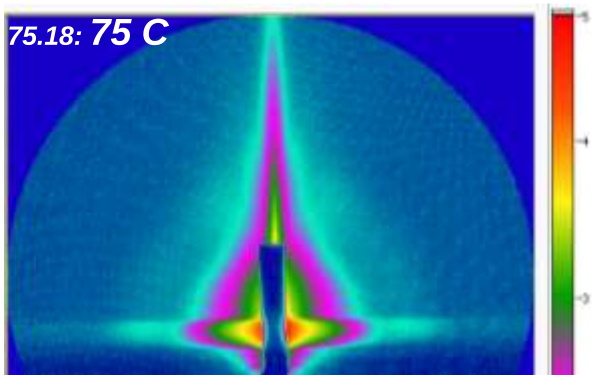
L. M. Molina et al., **Catalysis Today**, 2010, 160, 116.

Shape changes with Ag nanoparticles in propylene epoxidation

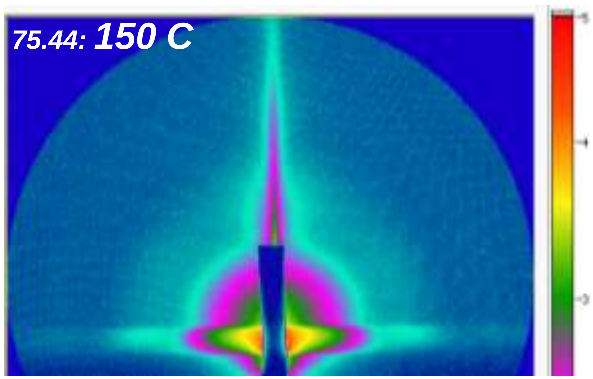
Under ~1 atm. pressure of 1.0% propylene and 0.5% oxygen in He
On 6 cycle Al2O3 over SiO2/Si with an initial cluster size ~6nm

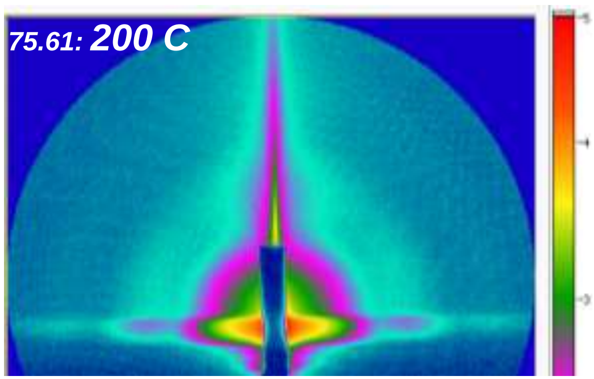


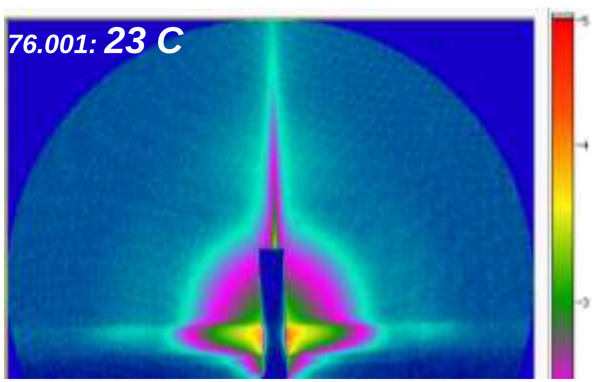




- change of the wetting angle
- onset of change of aspect ratio



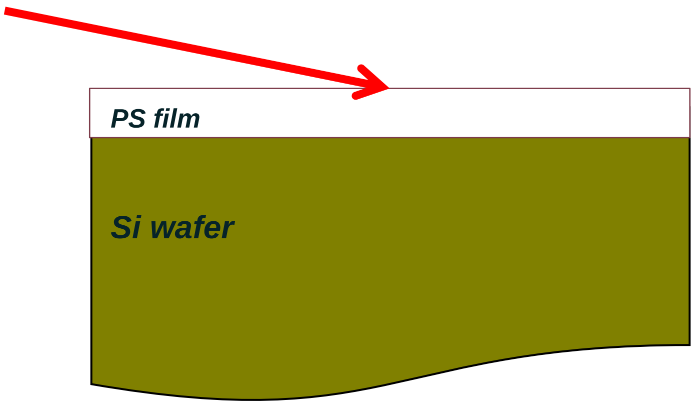




- particle shape transformation to spherical form
- particles remain spherical after 4 hrs reaction and cooling back to 23 C

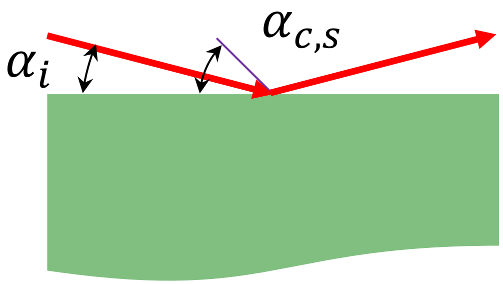
The effect of small incidence angle
2. Critical angle

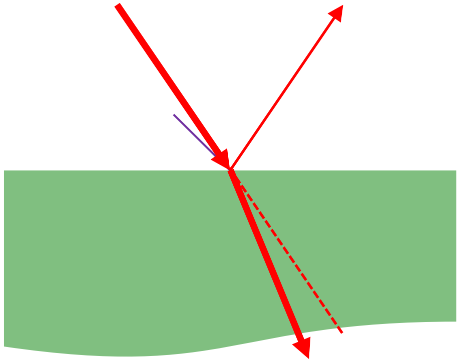
$$\alpha_c = \lambda(r_e \bar{\rho}/\pi)^{1/2}$$

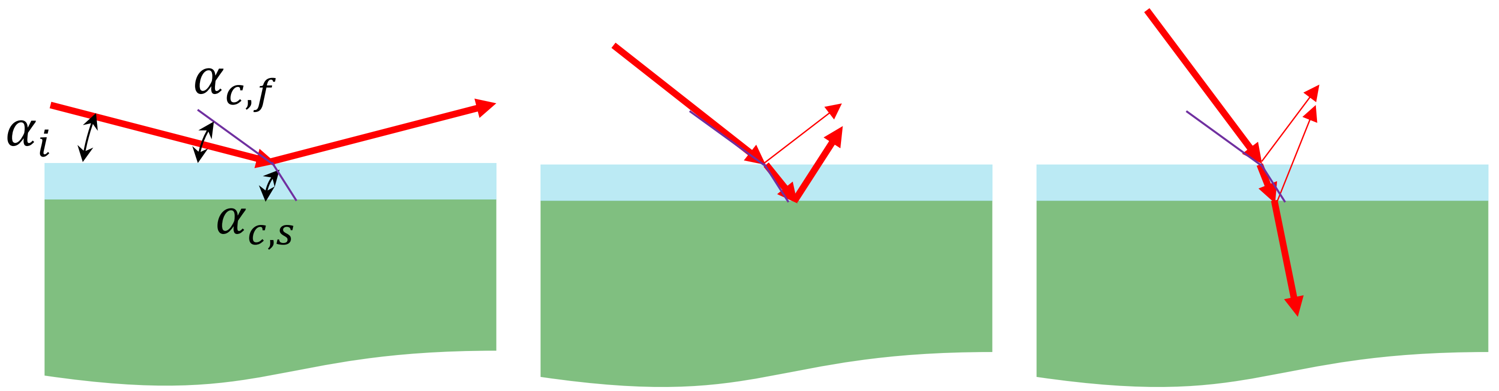


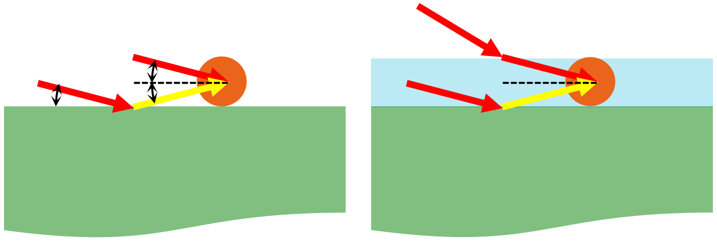
Electron density	Critical angle at 8keV
0.32 e/Å^3	0.150 degree
0.70 e/Å^3	0.223 degree

Critical angles



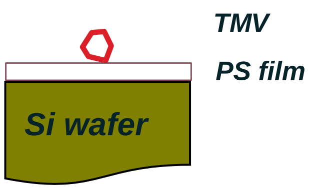


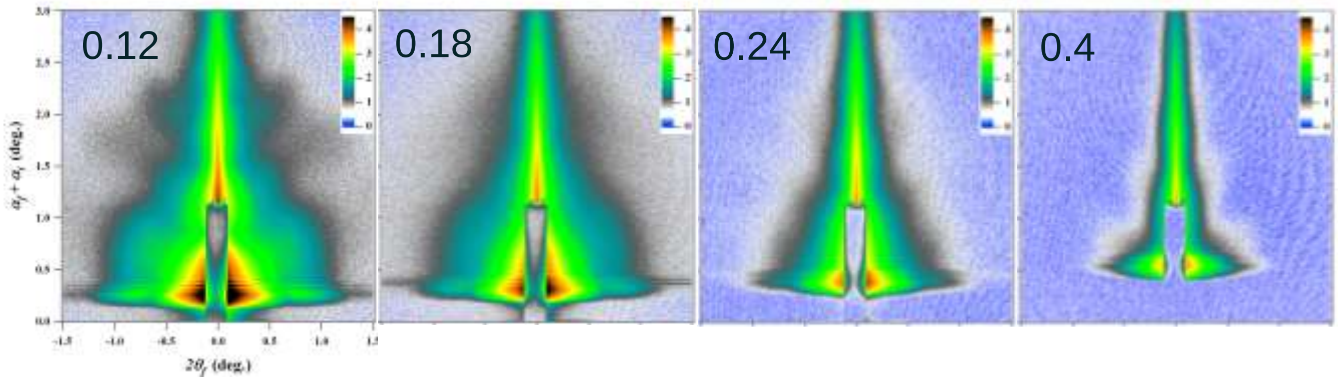

$\alpha_{c,f}$
α_i
$\alpha_{c,s}$



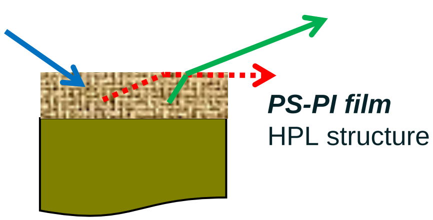
Vary the incident angle!!

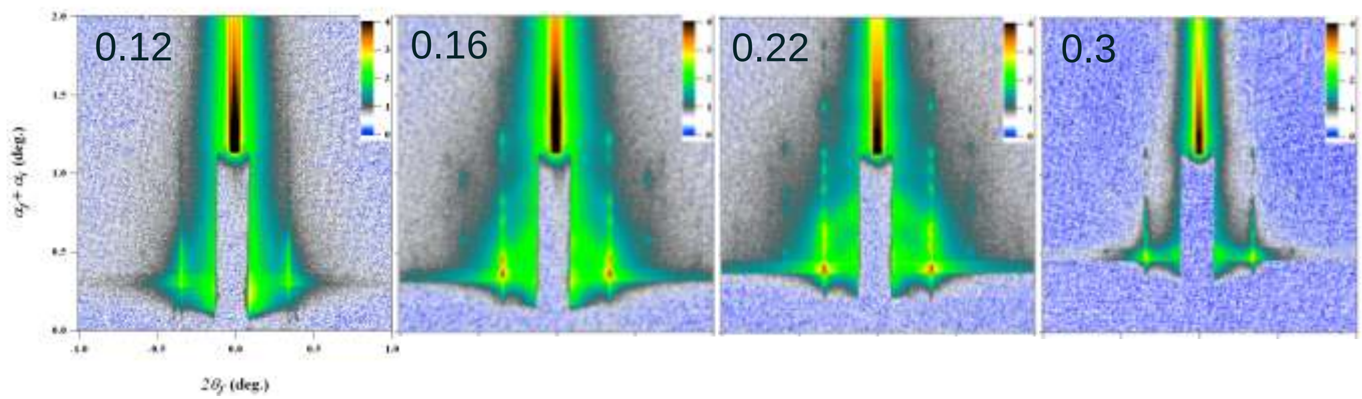
X-ray energy: 7.38keV
Critical angles of PS and PS-PI block copolymer film and Si wafer ~ 0.16° and 0.25°, respectively.





As long as the incident angle is smaller than the critical angle of substrate, particle scattering will be detected.
If overshooting is not an issue , the smaller incident angle is the better because smaller q is accessible.

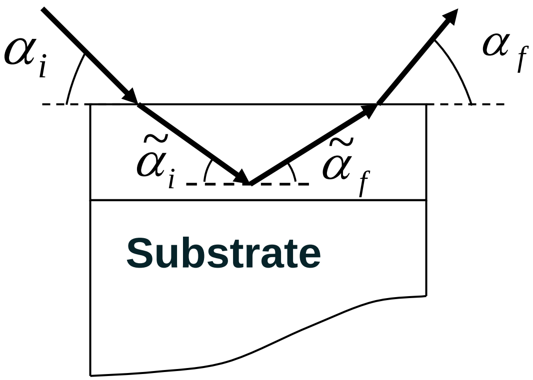




If the incident angle is smaller than the critical angle of film, x-ray can only scan top surface of film
If the exit angle is smaller than the critical angle of film, scattered x-ray practically cannot be detected.

B. Lee et al. **J. Appl. Cryst.** 2008, 41, 134-142.
B. Lee et al. **J. Appl. Cryst.** 2007, 40, 496-504.

The effect of a small incident angle
3. Refraction

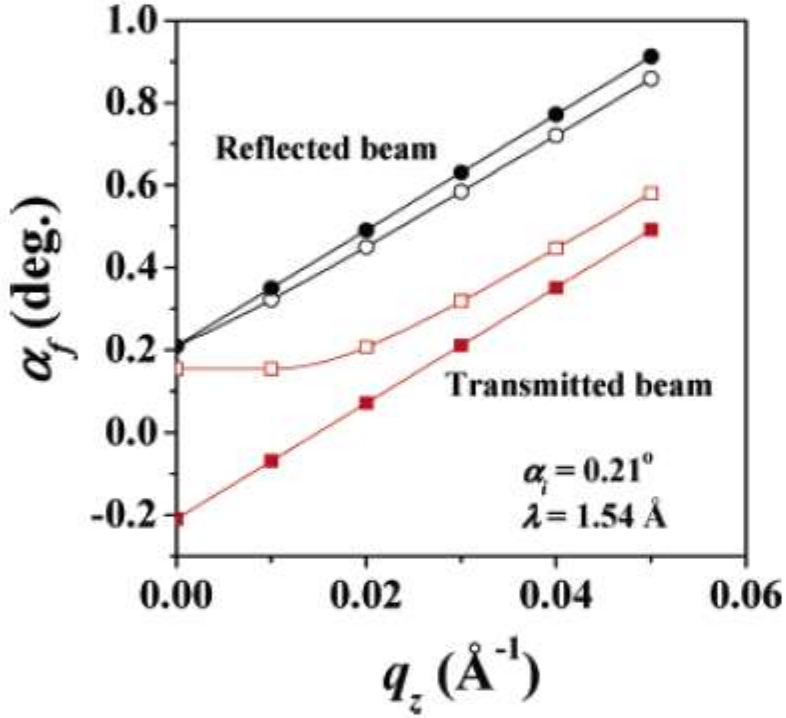


$$n_f = 1 - \delta + i\beta \equiv 1 - \alpha_c^2/2 + i\beta$$

$$\alpha_c = \lambda(r_e\bar{\rho}/\pi)^{1/2}$$

$$n_f \cos\tilde{\alpha} = \cos\alpha$$

How much x-ray will be refracted in a polymer film



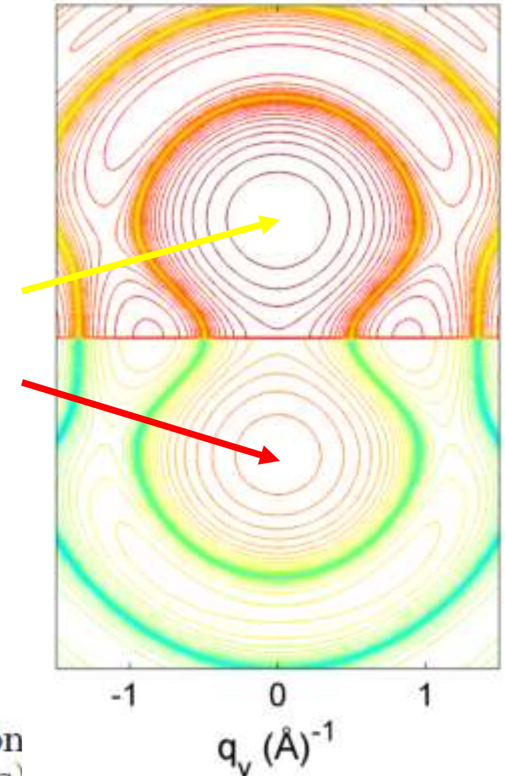
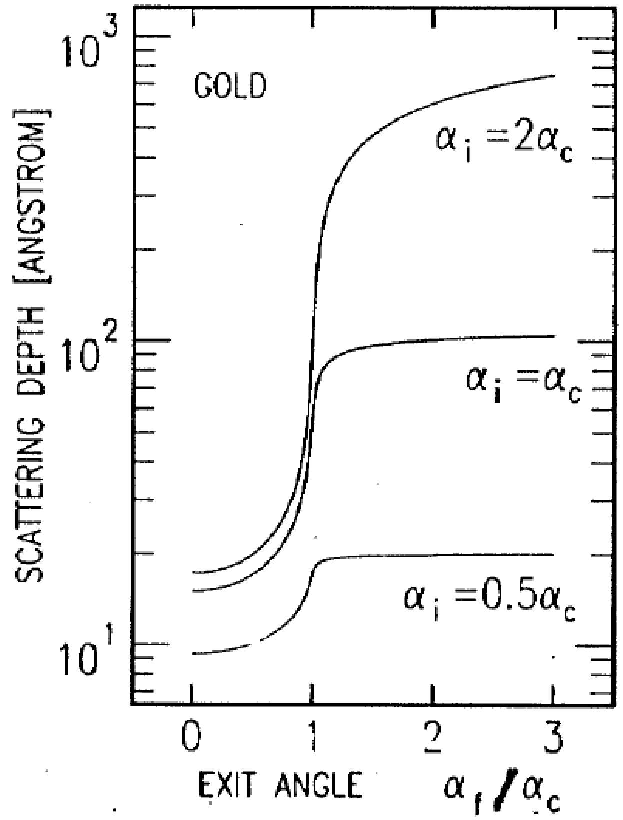


Figure 6. Relations between q_z and α_f of the diffraction due to the reflected (circles) and transmitted (squares) beams: the filled and open symbols denote the diffraction peaks without and with correction for the refraction effect, respectively.

B. Lee et al. Macromolecules, 2005, 38 (10), pp 4311–4323

Penetration depth

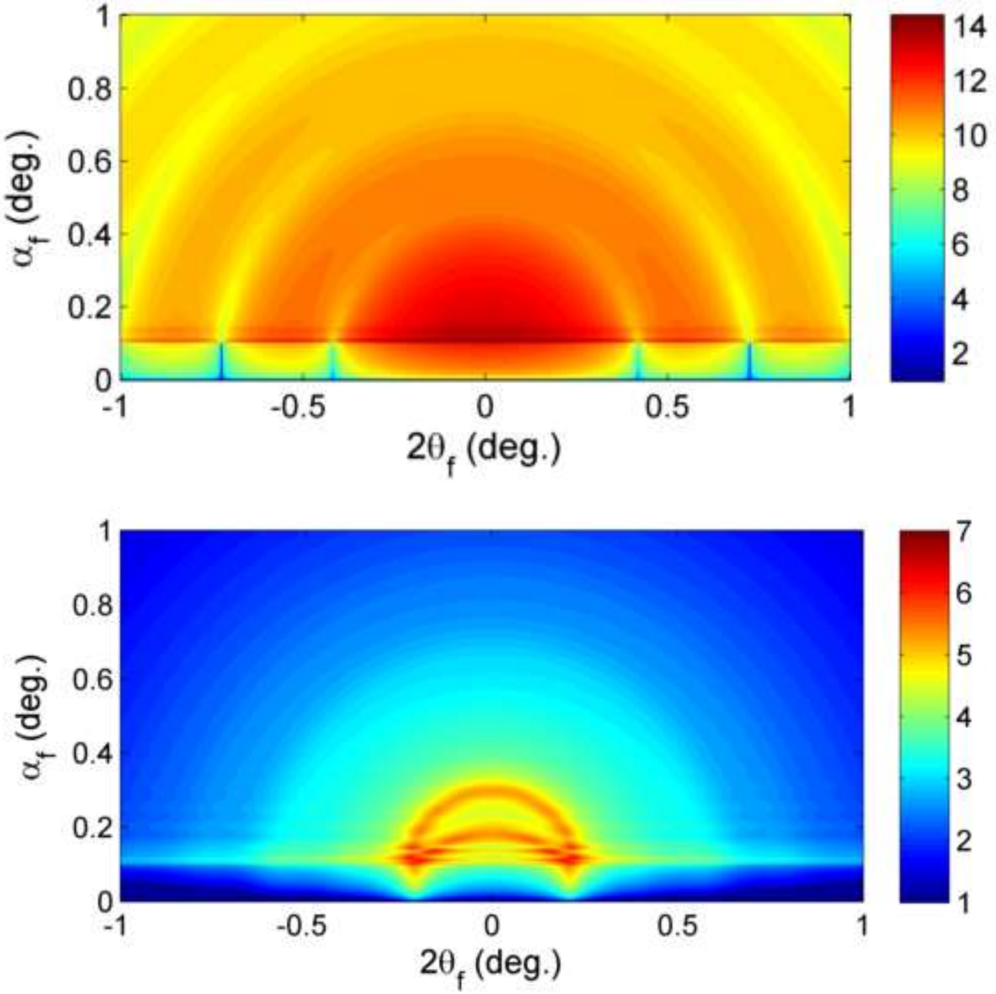


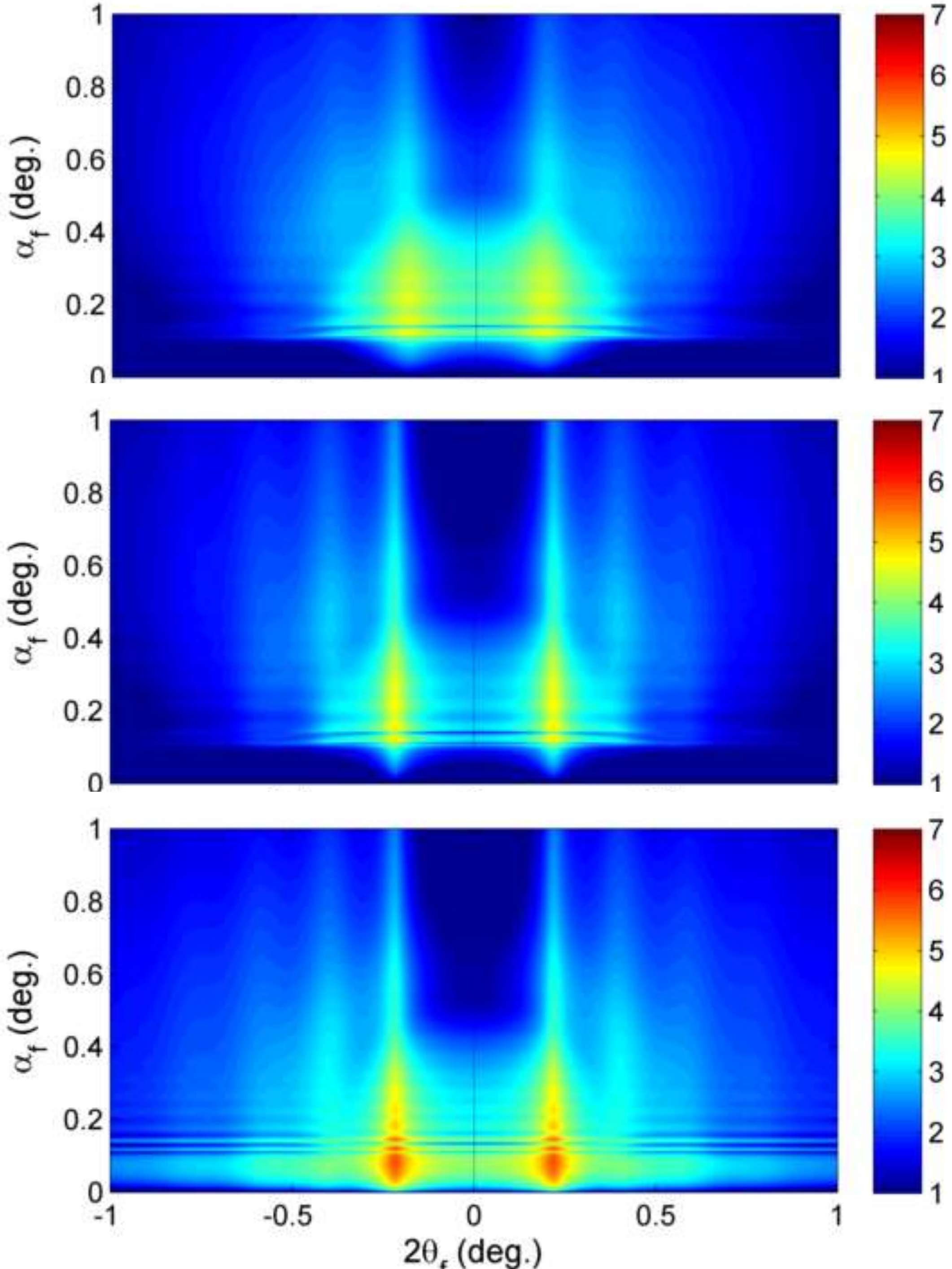
$$\alpha_c = \lambda(r_e \bar{\rho}/\pi)^{1/2}$$

Figure 21. Universal curves of the variation of scattering depth Λ with incidence and exit angles α_i and α_f, expressed as multiples of α_c. The units of the vertical scale depend in general on the photoelectric absorption of the sample, but have been calculated here for gold at $\lambda = 1.5$ Å using equation (48).

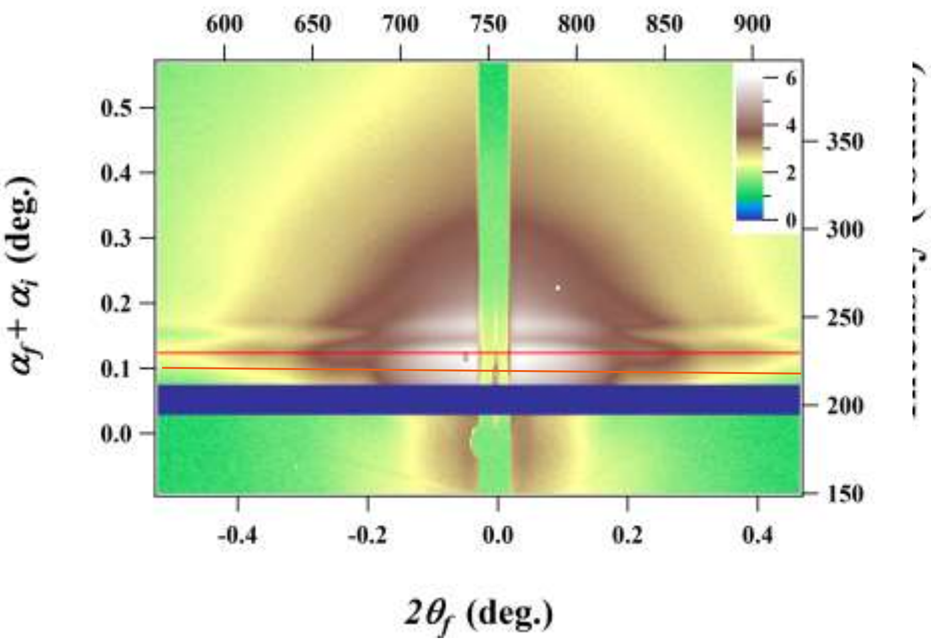
I.K. Robinson, D. J. Tweet Rep.Prog.Phys. 55(1992), 599
R. Feidenhans'l Surf. Sci. Rep. 10(1989) 105.

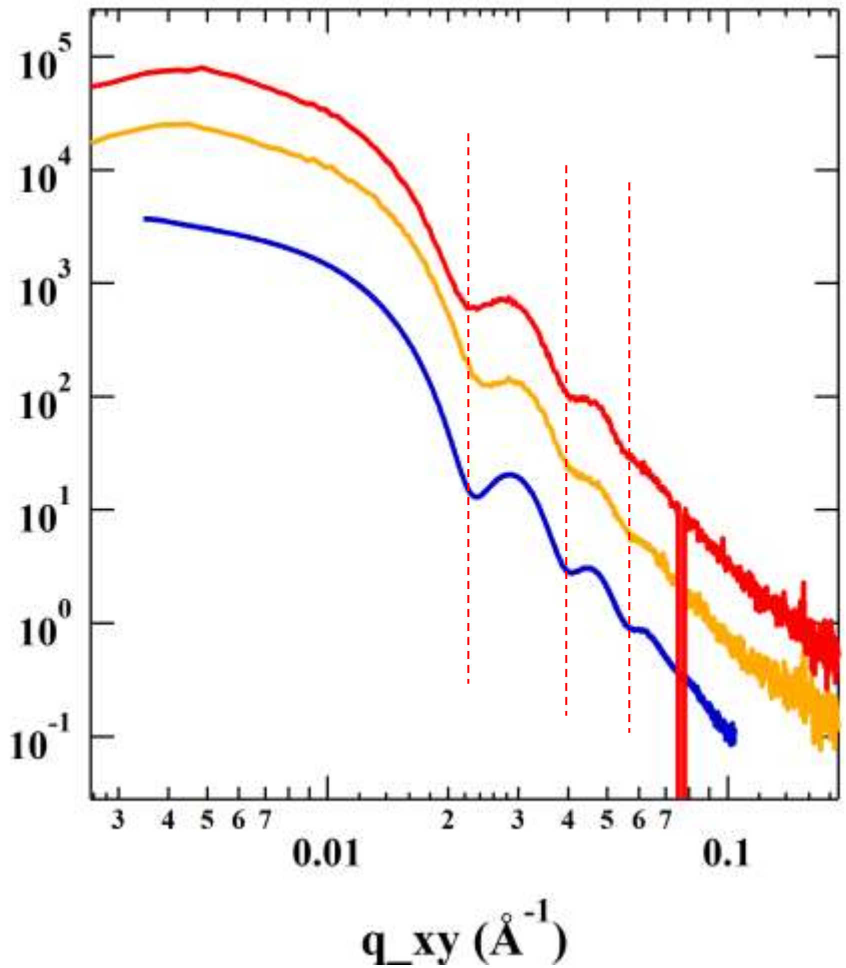
Quiz




α_f (deg.)
$2\theta_f$ (deg.)

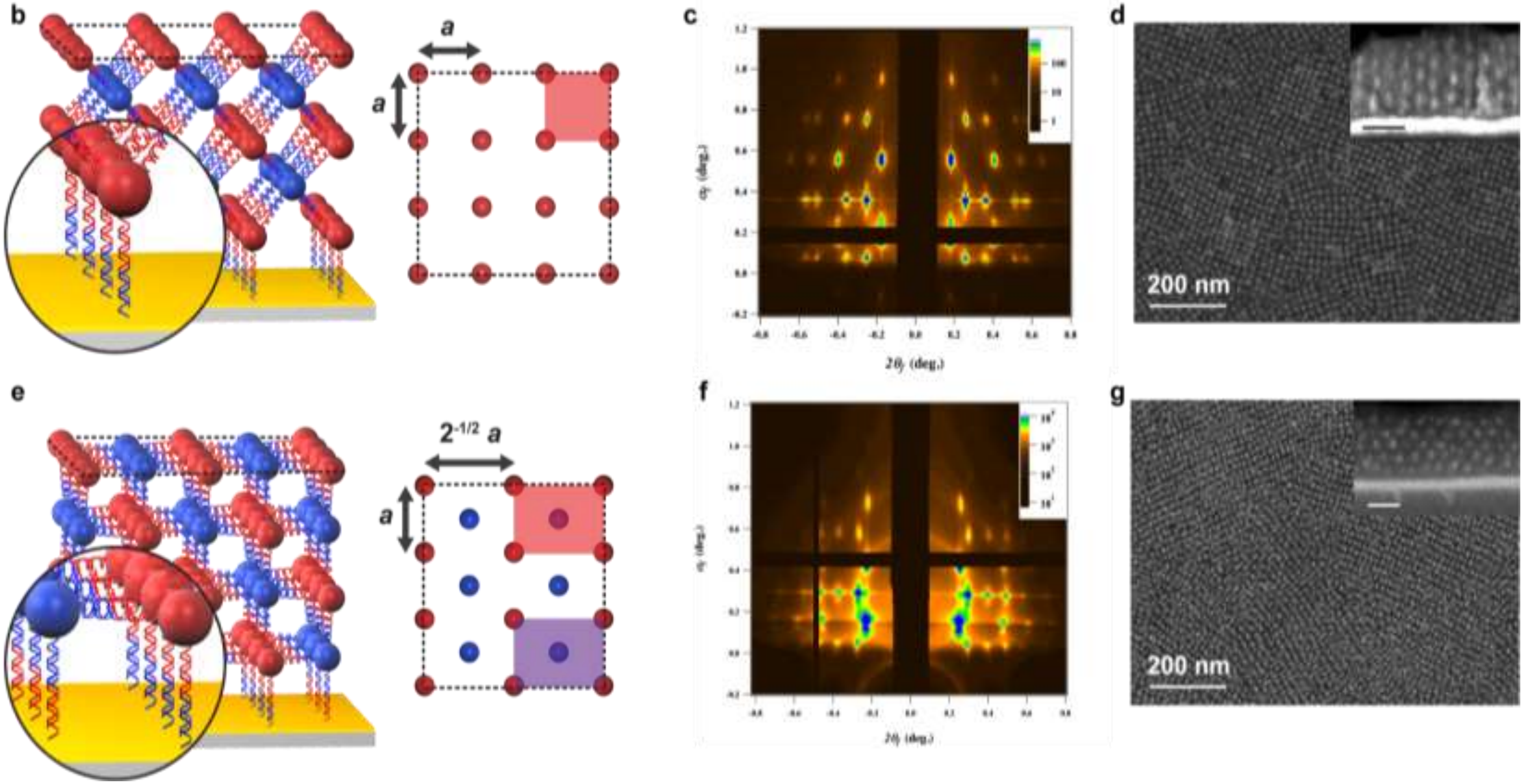
GISAXS vs SAXS : 40nm AuNp



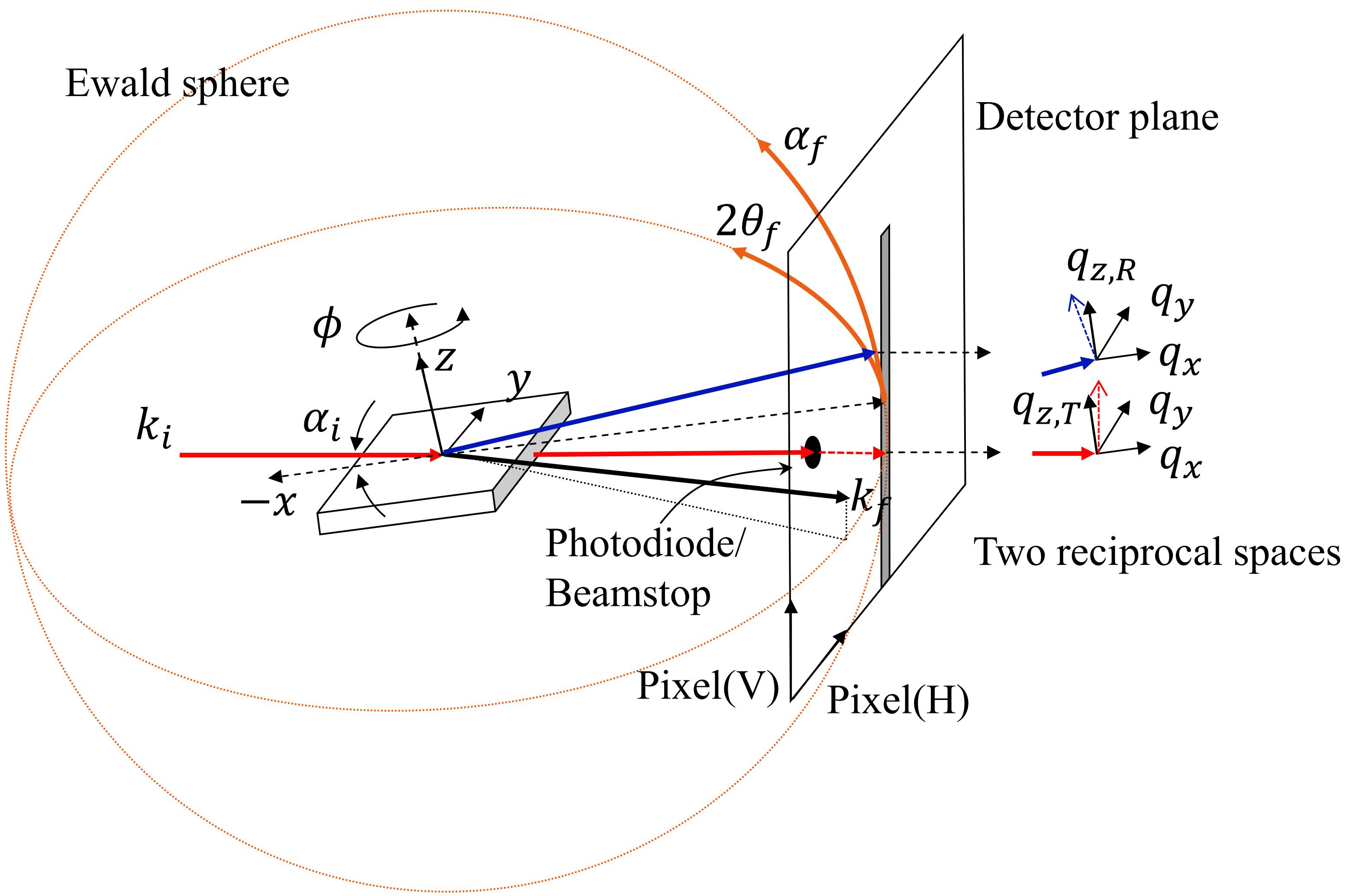


Diffraction from lattice

2D powder
BCC – 100 vs 110 orientation

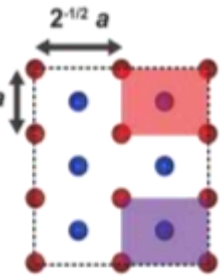


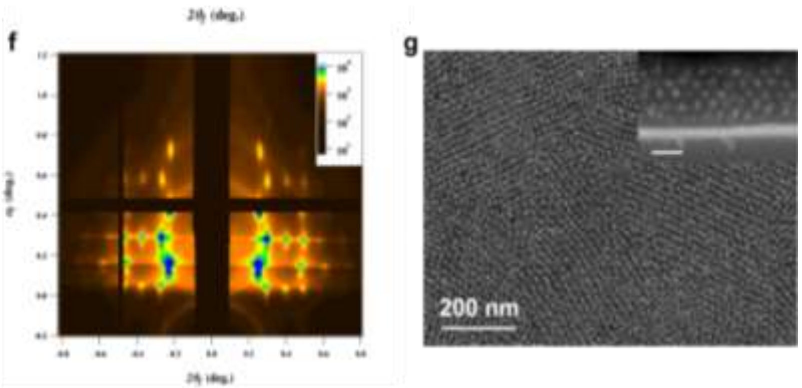
A. Senesi, B. Lee et al. **Angew. Chem. Int. Ed.**, 2013, 52(26), 6624–6628

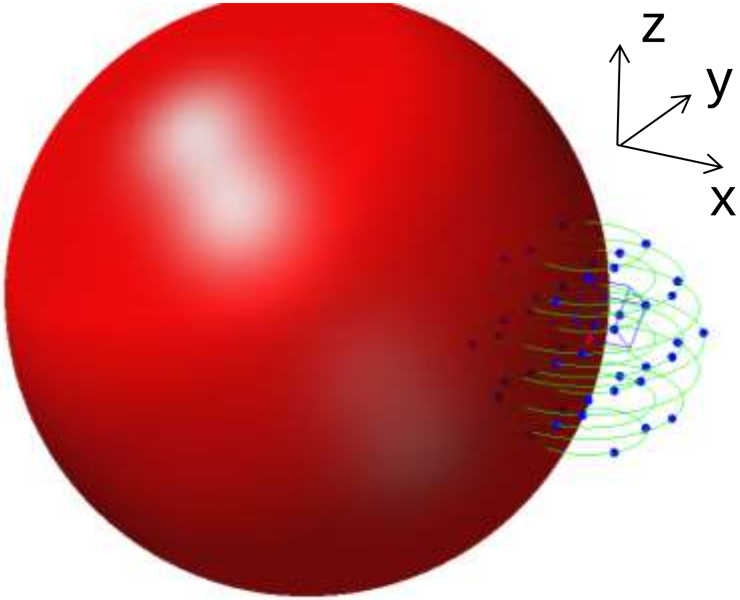


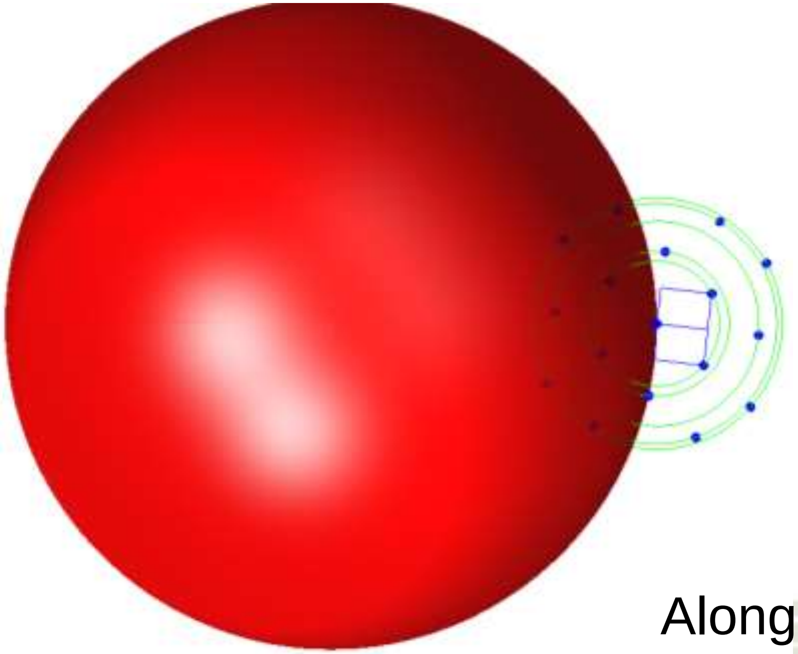
Ewald sphere
Detector plane
α_f
$2\theta_f$
ϕ
z
y
k_i
α_i
$-x$
k_f
Photodiode/
Beamstop
Pixel(V)
Pixel(H)
$q_{z,R}$
q_y
q_x
$q_{z,T}$
q_y
q_x
Two reciprocal spaces

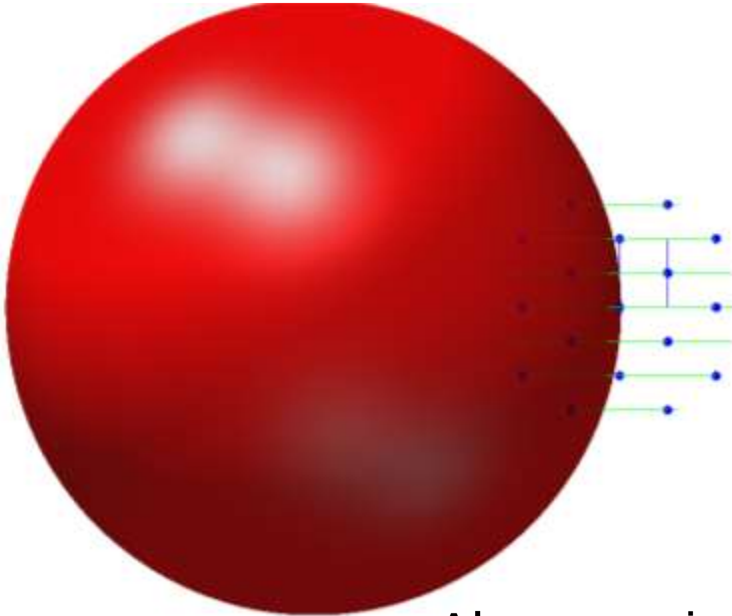
BCC 110 orientation







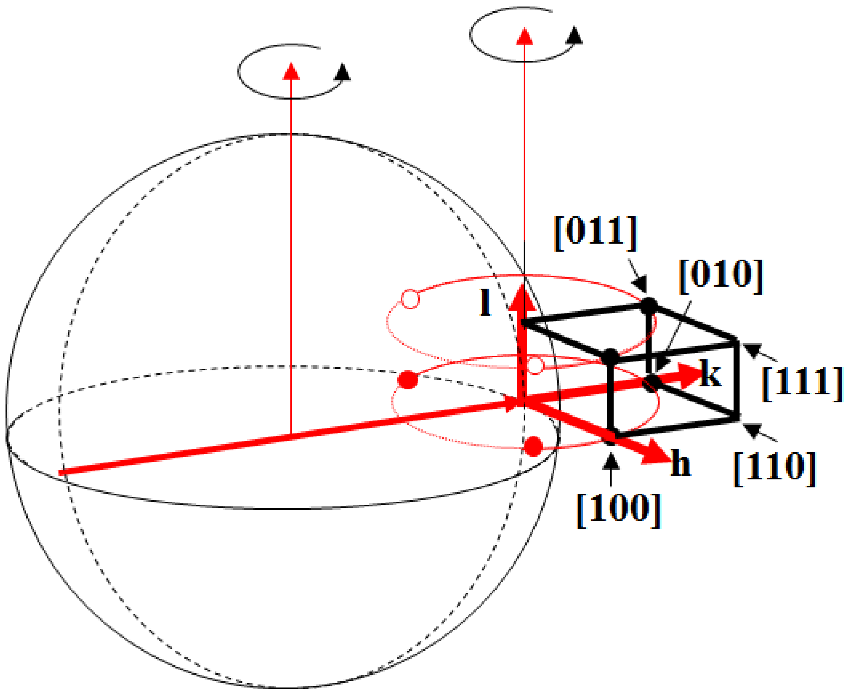


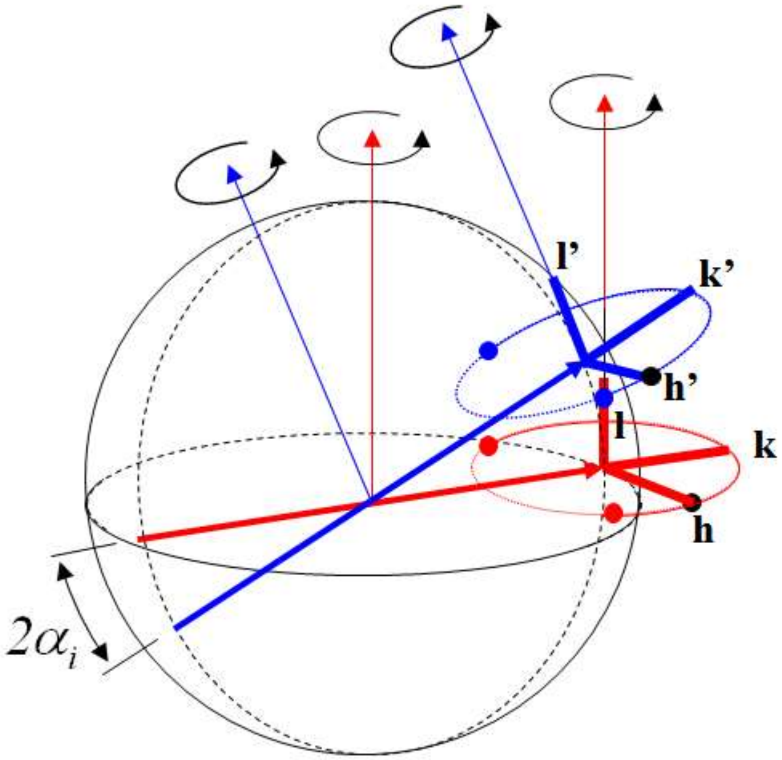


Along z axis

Along y axis

Ewald sphere





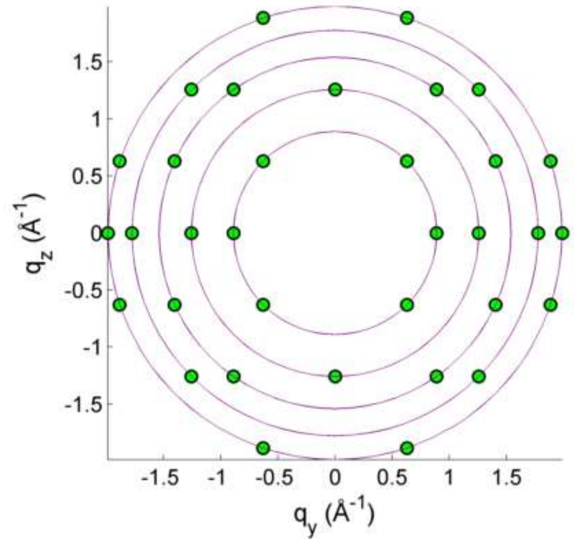
Two-beam effect

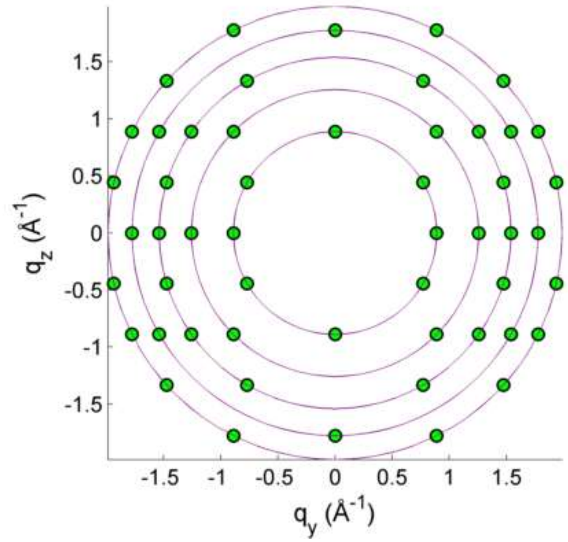
Refraction correction

Crystal orientation matrix

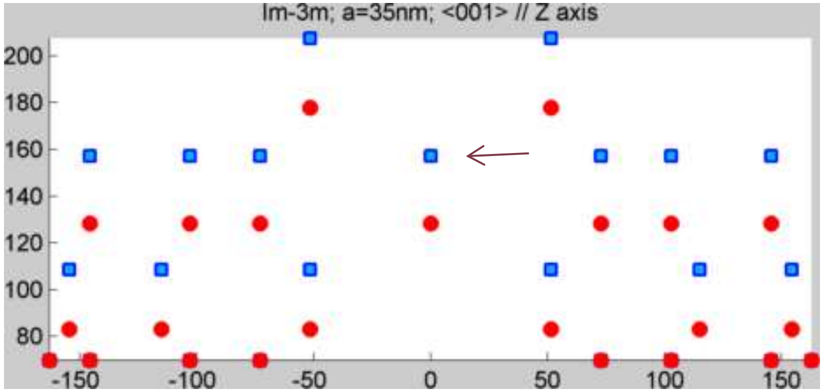
Penetration depth

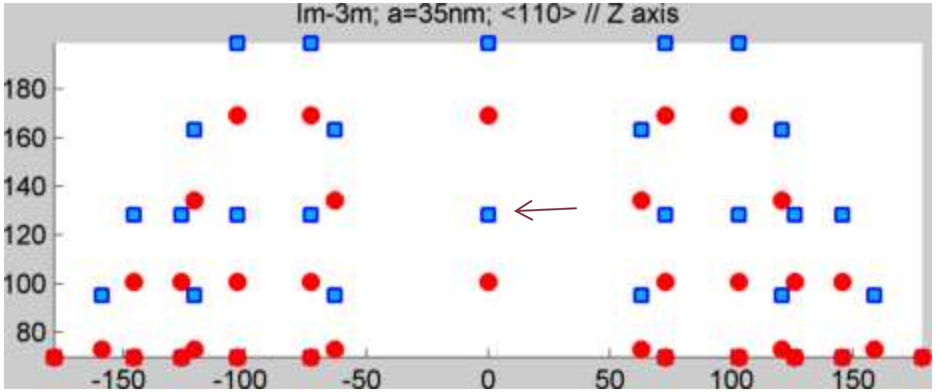
BCC : 100 vs 110



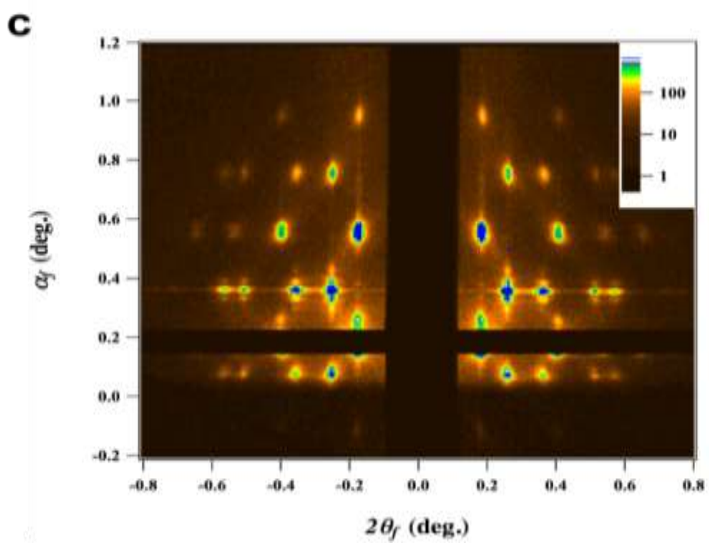


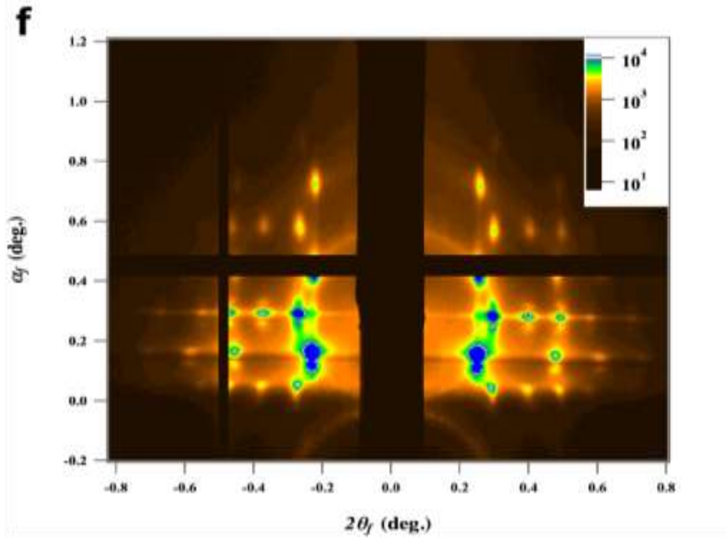
BCC : 100 vs 110





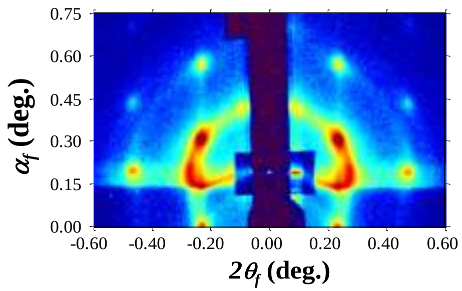
BCC : 100 vs 110

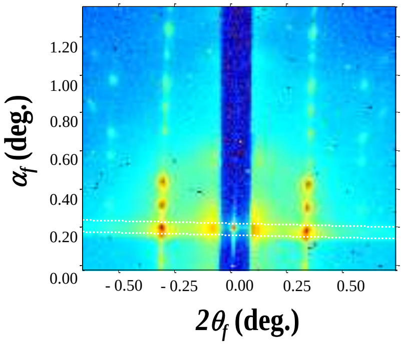


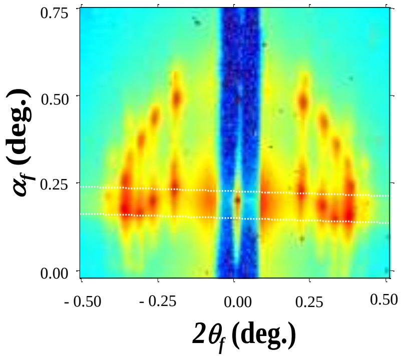


A. Senesi, B. Lee et al. **Angew. Chem. Int. Ed.**, 2013, 52(26), 6624–6628

Diffractions from block copolymer films





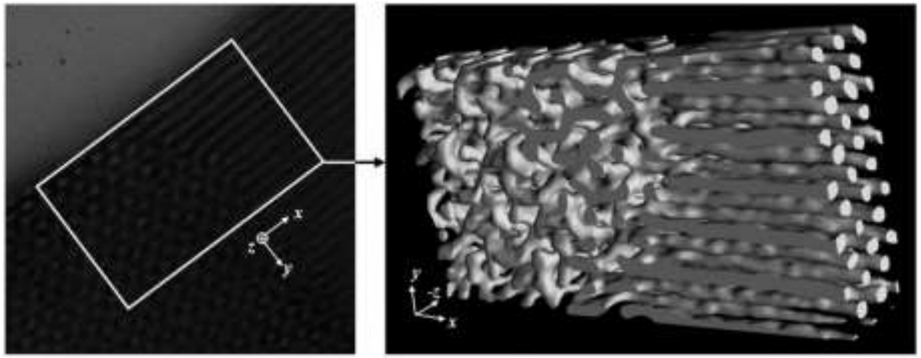


Hexagonal Cylinder

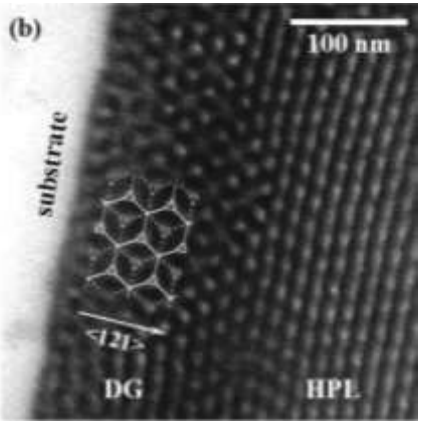
Hexagonally perforated layer

Gyroid : Cubic(*Ia3d*)

Lee et al. Macromolecules, 2005, 38, 4311

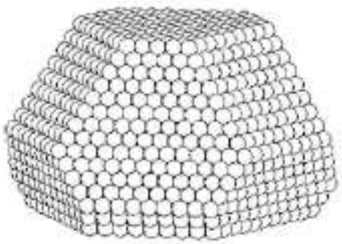


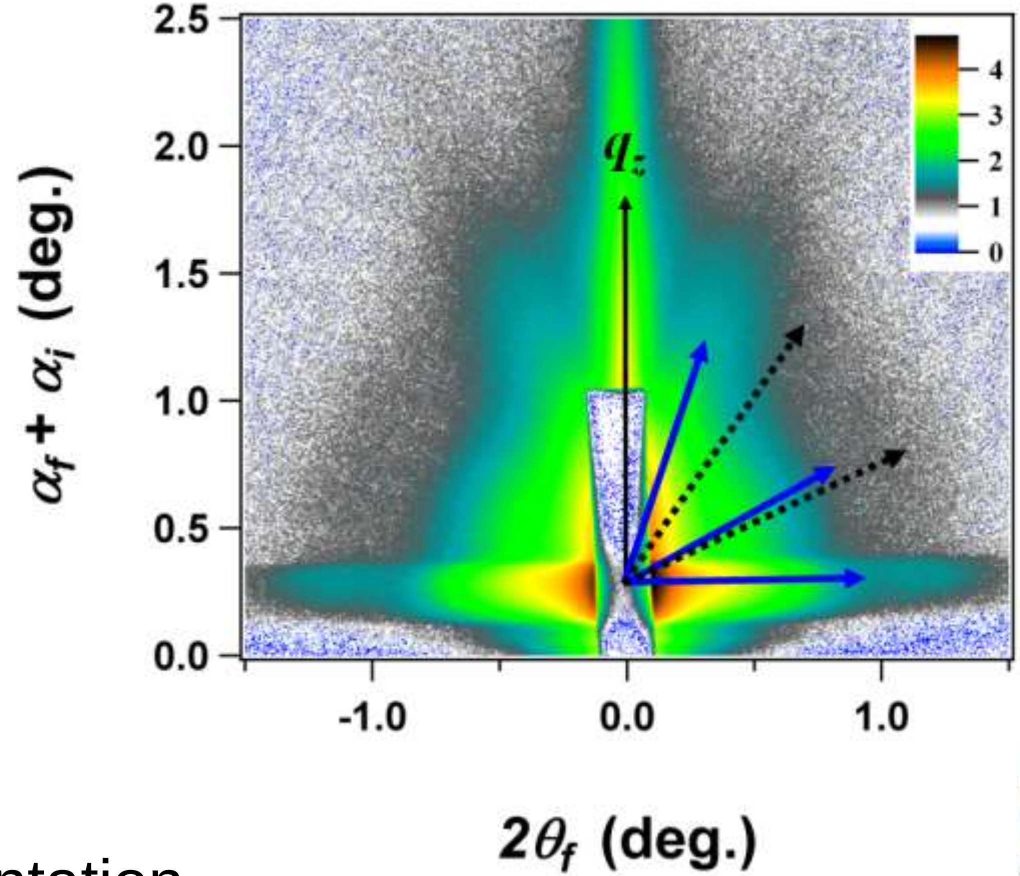
H.-W.Park et al. J. Am. Chem. Soc., **2009**, *131* (1), pp 46–47



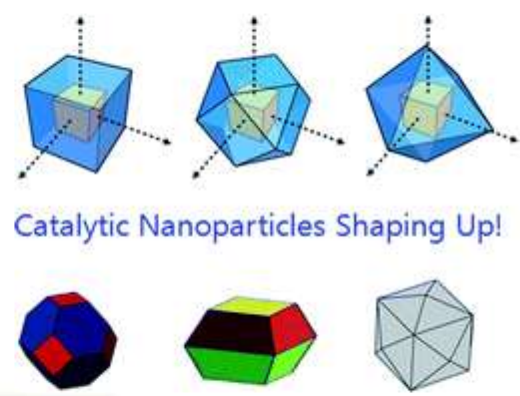
H.-W. Park et al. Macromolecules, 2007, 40 (7), pp 2603–2605

Facet analysis



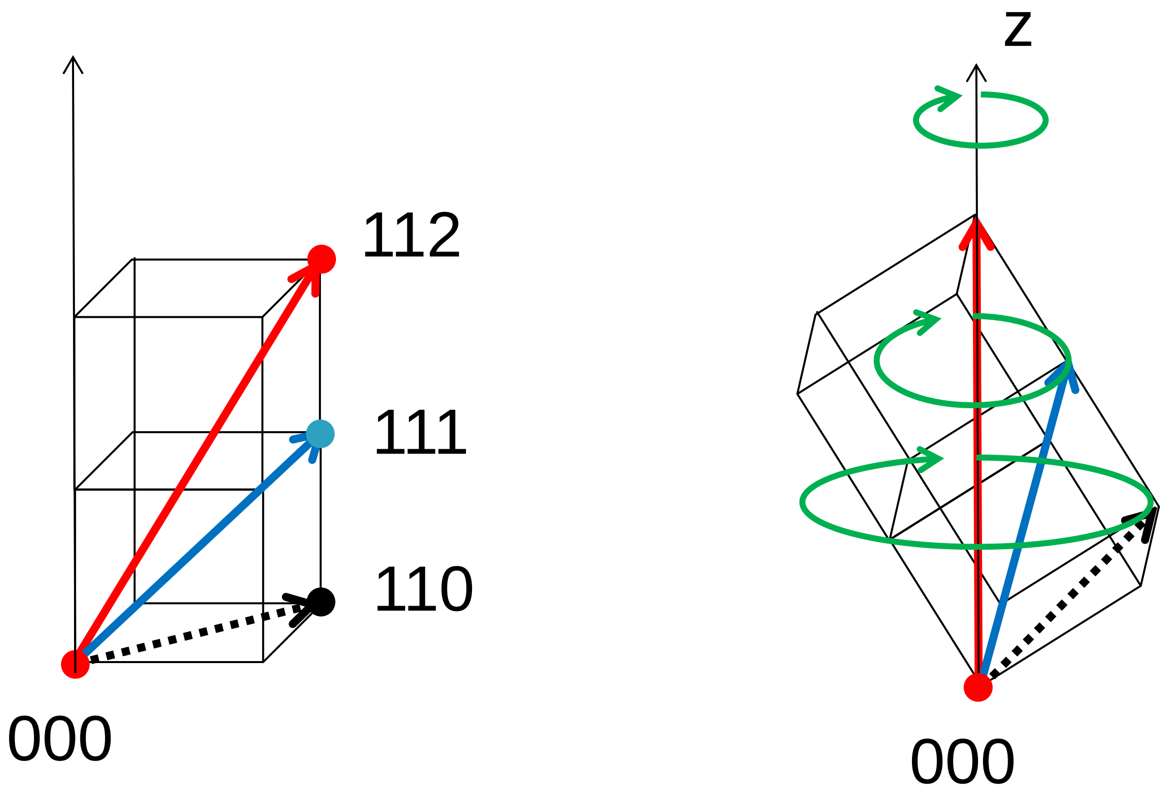


112 orientation
111 : 19.5, 61.9, and 90^o
110 : dotted arrows

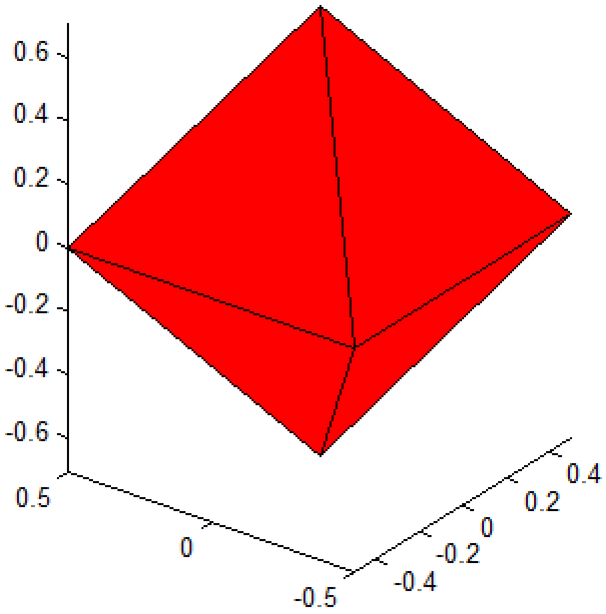


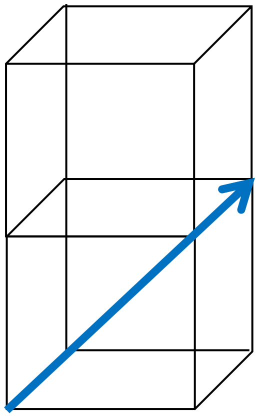
L. M. Molina et al., **Catalysis Today**, 2010, 160, 116.

2D powder with 112 orientation

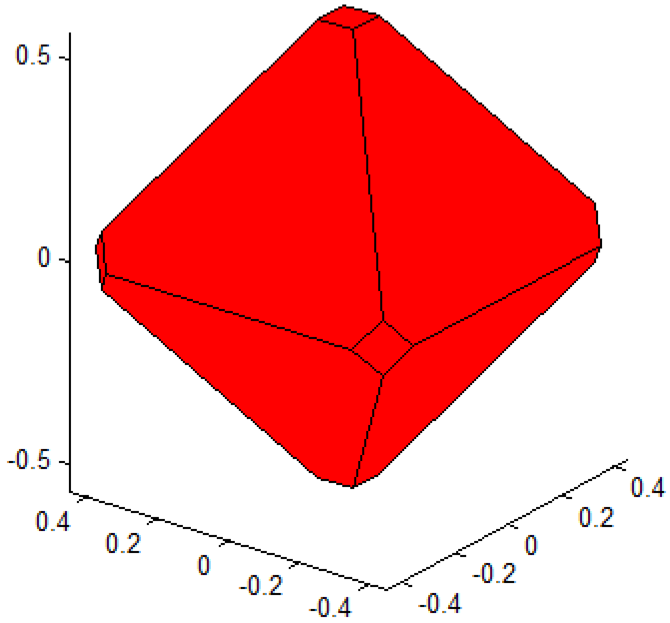


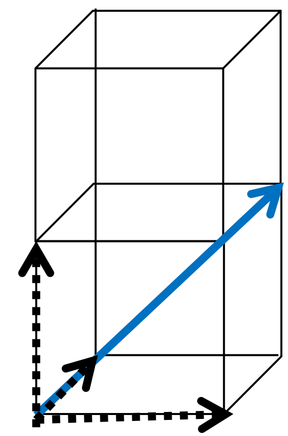
Octahedron



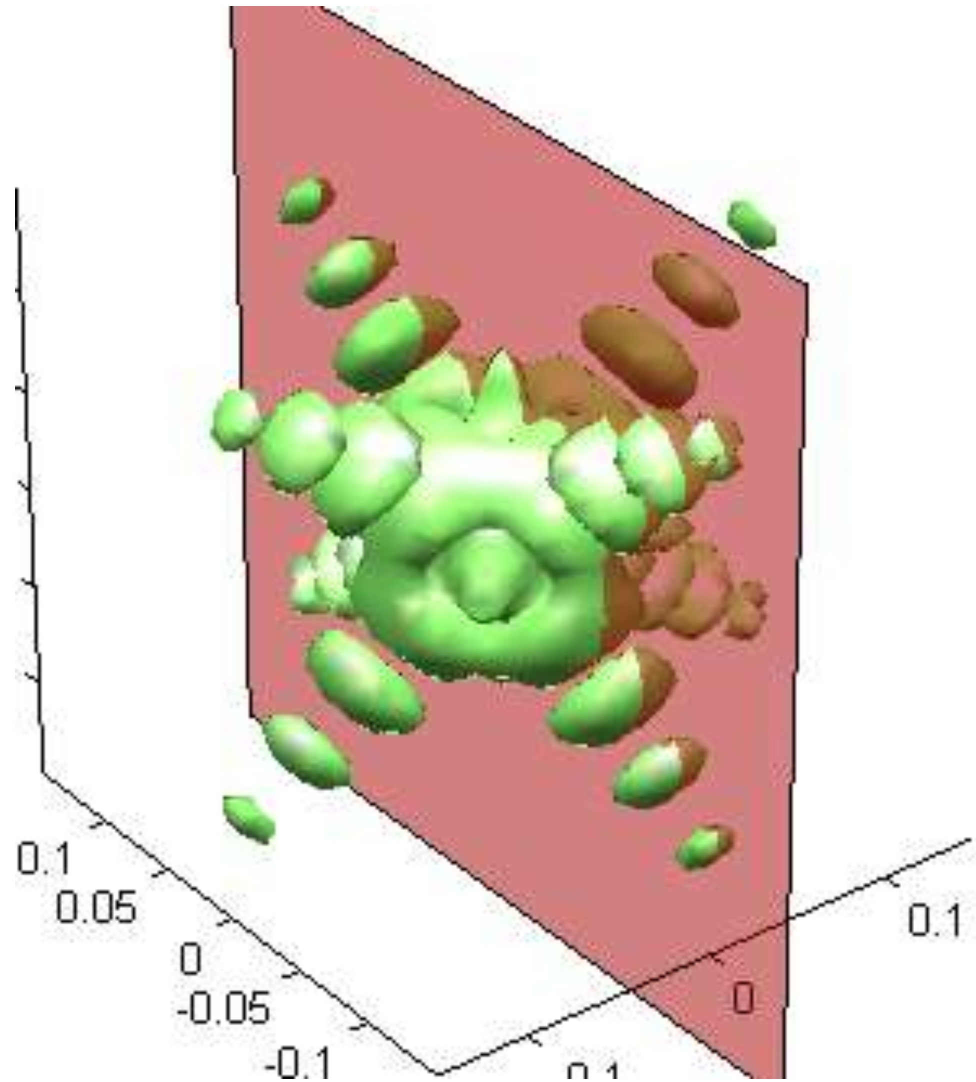


Truncated Octahedron

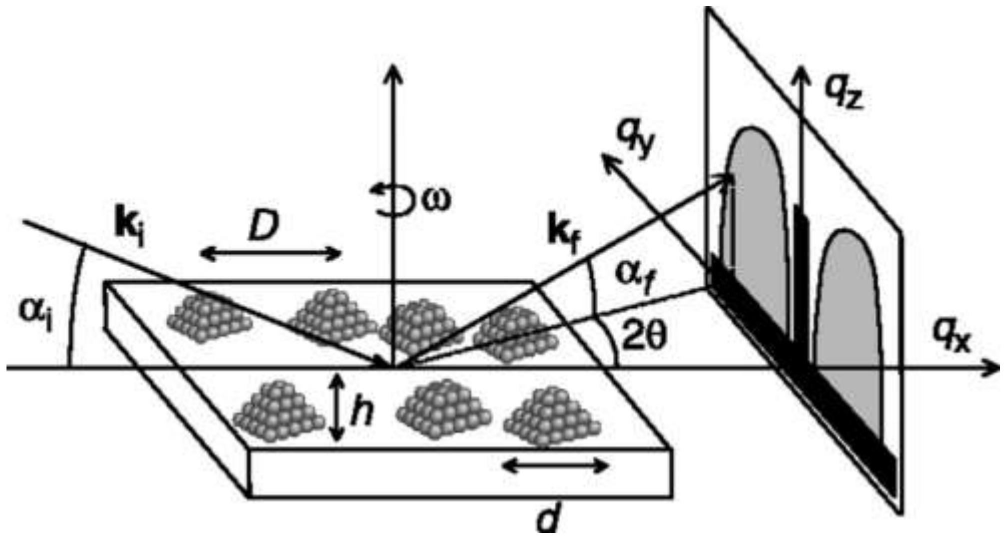




Octahedron scattering in the reciprocal space



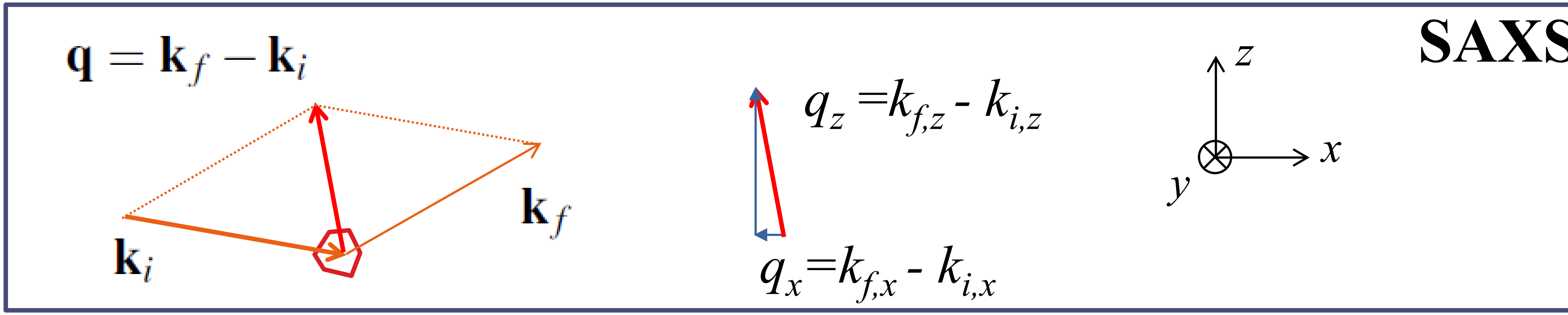
Quantitative calculation

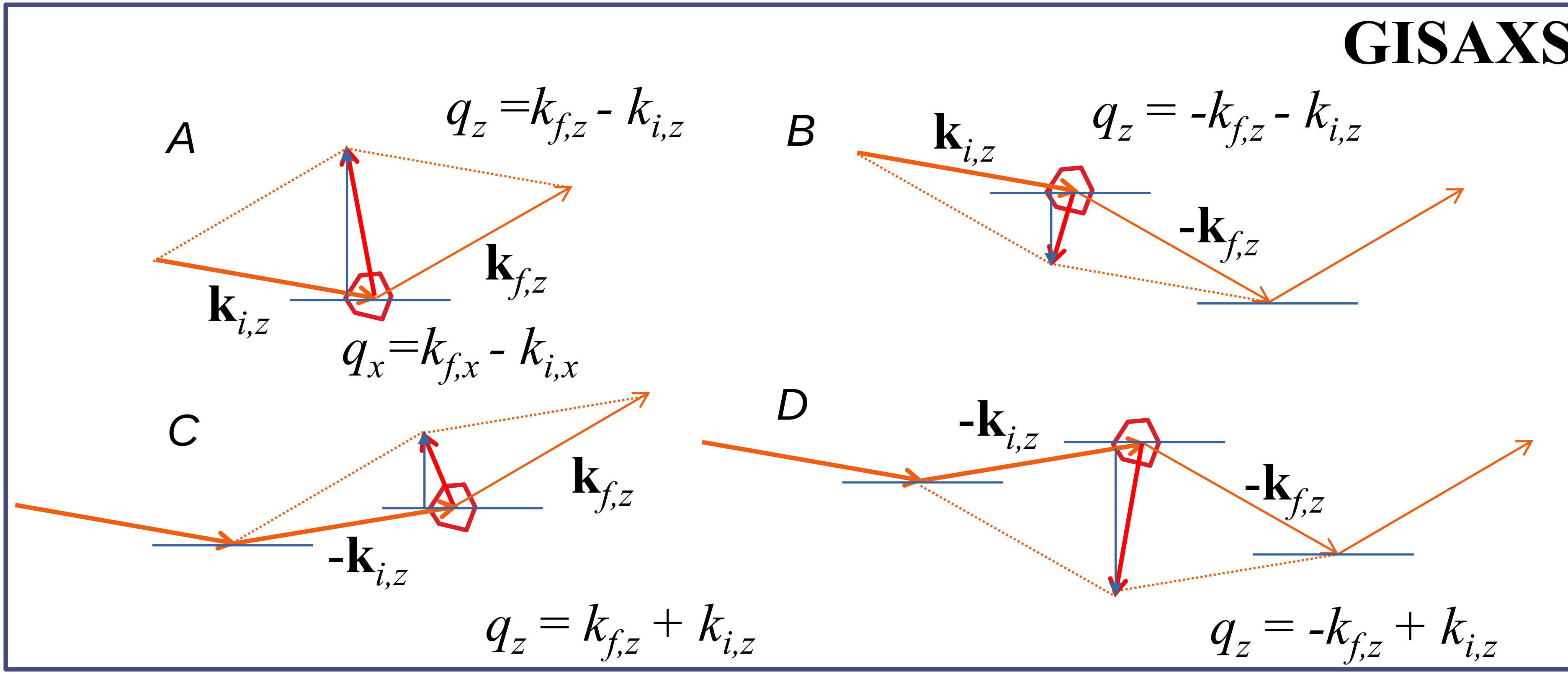


$$\begin{pmatrix} q_x \\ q_y \\ q_{z,X} \end{pmatrix} = n_f k_0 \begin{pmatrix} \cos\tilde{\alpha}_f \cos 2\theta_f - \cos\tilde{\alpha}_i \\ \cos\tilde{\alpha}_f \sin 2\theta_f \\ \sin\tilde{\alpha}_f \pm \sin\tilde{\alpha}_i \end{pmatrix}$$

where X = t or r for + or –, and the tilde indicates the refracted angle.

Definition of q : Four q's in GISAXS due to the reflection



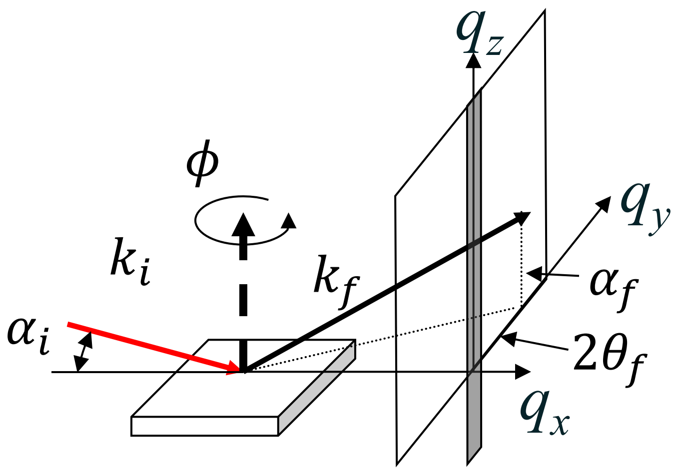


Full DWBA formulae

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = r^2 \psi_{\mathrm{sc}}(r)\psi^*_{\mathrm{sc}}(r)$$

$$= A \Big| T_{\mathrm{i}} T_{\mathrm{f}} F(\mathbf{q}_{||}, q_{z,\mathrm{t}}) + T_{\mathrm{i}} R_{\mathrm{f}} F(\mathbf{q}_{||}, -q_{z,\mathrm{r}})$$

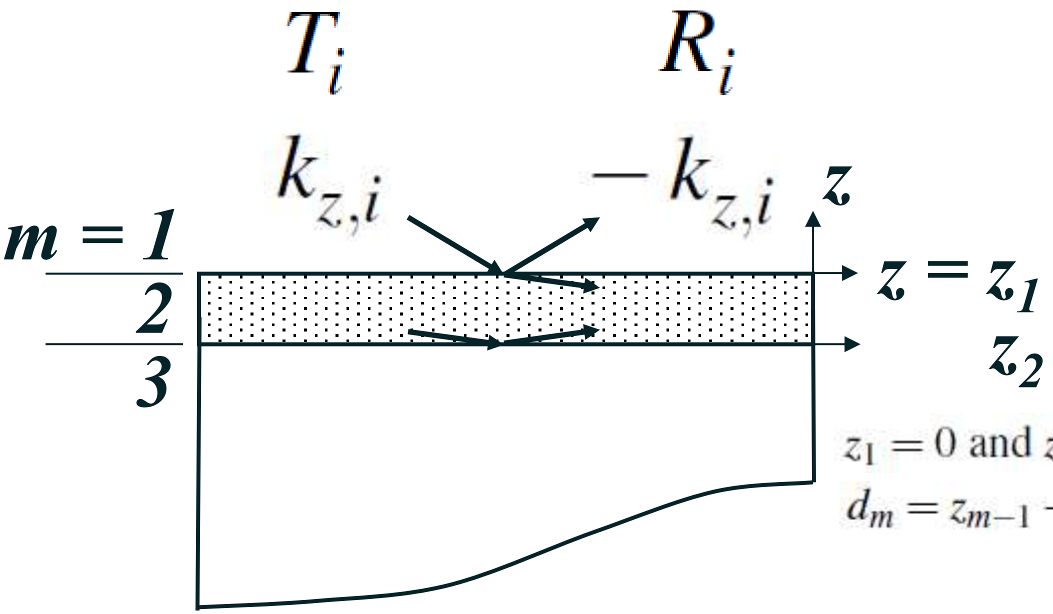
$$+ R_{\mathrm{i}} T_{\mathrm{f}} F(\mathbf{q}_{||}, q_{z,\mathrm{r}}) + R_{\mathrm{i}} R_{\mathrm{f}} F(\mathbf{q}_{||}, -q_{z,\mathrm{t}}) \Big|^2$$

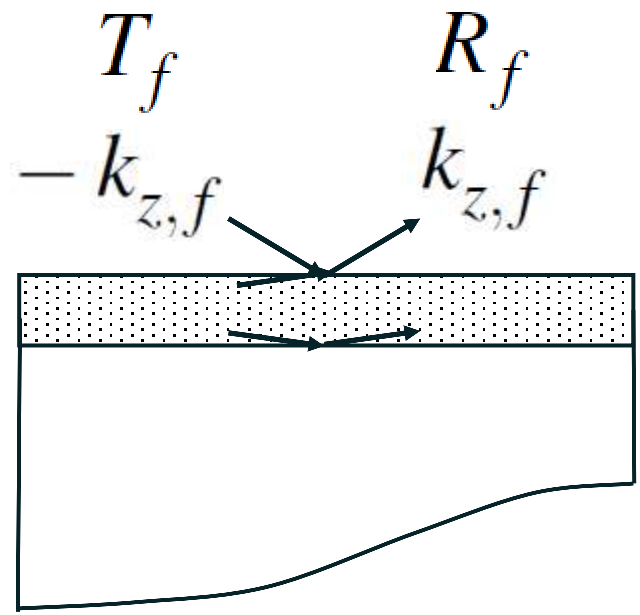


$$\mathbf{q}_{\mathrm{t}} = (\mathbf{q}_{||}, q_{z,\mathrm{t}})$$

$$\mathbf{q}_{\mathrm{r}} = (\mathbf{q}_{||}, q_{z,\mathrm{r}})$$

Fresnel's law (wave amplitude) and Snell's law (wave vector)





$z_1 = 0$ and $z_{m \neq 1} < 0$

$d_m = z_{m-1} - z_m > 0.$

$$\psi_i(\alpha_i) = T_i e^{ik_{z,i}z} + R_i e^{-ik_{z,i}z}$$

$$\psi_f(\alpha_f) = \left(T_f e^{-ik_{z,f}z} + R_i e^{ik_{z,f}z}\right)^*$$

$$k_{z,i,m} = -k_0\sqrt{n_m^2 - \cos^2\alpha_i}$$

$$k_{z,f,m} = k_0\sqrt{n_m^2 - \cos^2\alpha_f}$$

$T_1 = 1$ and $R_N = 0.$

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Fresnel's law (wave amplitude) and Snell's law (wave vector)

The Fresnel coefficients at the interface between layers m and $m+1$ are

$$r_{m,m+1} = \frac{k_{z,m} - k_{z,m+1}}{k_{z,m} + k_{z,m+1}}$$
$$t_{m,m+1} = \frac{2k_{z,m}}{k_{z,m} + k_{z,m+1}},$$

$$X_m = \frac{R_m}{T_m} = e^{2ik_{z,m}z_m}\left(\frac{r_{m,m+1} + X_{m+1}e^{2ik_{z,m+1}z_m}}{1 + r_{m,m+1}X_{m+1}e^{-2ik_{z,m+1}z_m}}\right)$$

$$R_{m+1} = \frac{1}{t_{m+1,m}}\left(T_m r_{m+1,m} e^{i(k_{z,m+1}+k_{z,m})z_m} + R_m e^{i(k_{z,m+1}-k_{z,m})z_m}\right)$$

$$T_{m+1} = \frac{1}{t_{m+1,m}}\left(T_m e^{-i(k_{z,m+1}-k_{z,m})z_m} + R_m r_{m+1,m} e^{-i(k_{z,m+1}+k_{z,m})z_m}\right)$$

$$X_m = \frac{R_m}{T_m} = e^{-2ik_{z,m}z_m}\left(\frac{r_{m,m+1} + X_{m+1}e^{2ik_{z,m+1}z_m}}{1 + r_{m,m+1}X_{m+1}e^{2ik_{z,m+1}z_m}}\right)$$

$$R_{m+1} = \frac{1}{t_{m+1,m}}\left(T_m r_{m+1,m} e^{-i(k_{z,m+1}+k_{z,m})z_m} + R_m e^{-i(k_{z,m+1}-k_{z,m})z_m}\right)$$

$$T_{m+1} = \frac{1}{t_{m+1,m}}\left(T_m e^{i(k_{z,m+1}-k_{z,m})z_m} + R_m r_{m+1,m} e^{i(k_{z,m+1}+k_{z,m})z_m}\right),$$

Intensity and scattering vectors

$$\Psi_{sc,m}(R) = -\frac{e^{ik_0R}}{R}\int \Psi^*_{f,m}(\mathbf{r})V(\mathbf{r})\Psi_{i,m}(\mathbf{r})d\mathbf{r},$$

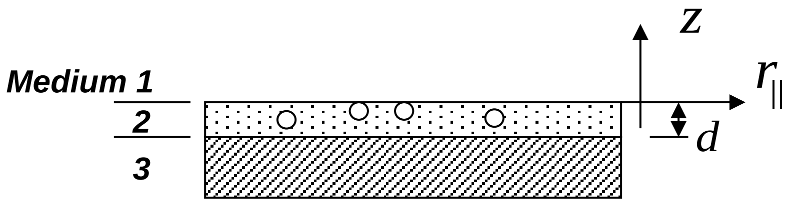
$$\Psi_{sc,m}(R) = \frac{e^{ik_0R}}{R}\Phi_m(\mathbf{q}),$$

$$\begin{aligned}\Phi_m(\mathbf{q}) = {} & T_{i,m}T_{f,m}A(\mathbf{q}_{||,m}, q_{t,z,m}) + T_{i,m}R_{f,m}A(\mathbf{q}_{||,m}, -q_{r,z,m}) \\ & + R_{i,m}T_{f,m}A(q_{||,m}, q_{r,z,m}) + R_{i,m}R_{f,m}A(\mathbf{q}_{||,m}, -q_{t,z,m}),\end{aligned}$$

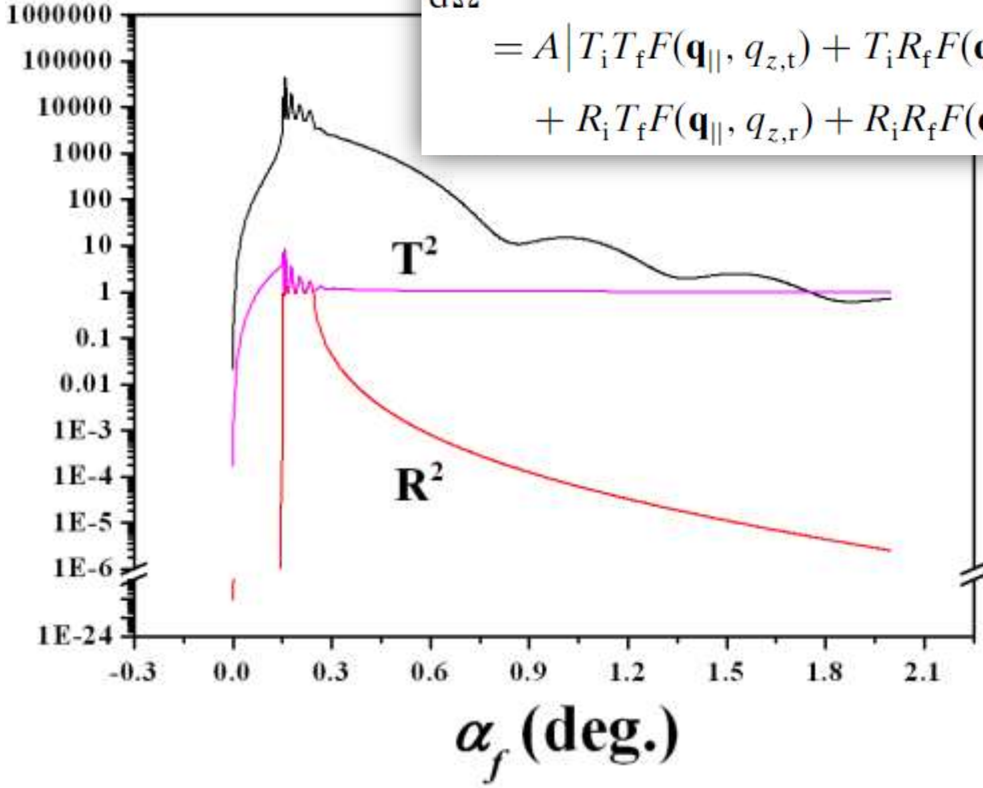
where $A(\mathbf{q})$ is the Fourier transform of V($\mathbf{r}$)

$$I(\mathbf{q}) = \sum_m R^2\Psi_{sc,m}(R)\Psi^*_{sc,m}(R) = \sum_m \Phi_m(\mathbf{q})\Phi^*_m(\mathbf{q})$$

Effect of wave amplitudes



$$\frac{d\sigma}{d\Omega} = r^2 \psi_{sc}(r)\psi^*_{sc}(r)$$
$$= A\left|T_i T_f F(\mathbf{q}_{||}, q_{z,t}) + T_i R_f F(\mathbf{q}_{||}, -q_{z,r}) + R_i T_f F(\mathbf{q}_{||}, q_{z,r}) + R_i R_f F(\mathbf{q}_{||}, -q_{z,t})\right|^2$$



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Softwares
http://ln-www.insp.upmc.fr/axe2/Oxydes/IsGISAXS/isgisaxs.htm
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http://sites.google.com/site/byeongdu/software